MERCURY

ANNUAL SURVEY COVERING THE YEAR 1976

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Mercury, Annual Survey covering the year 1975, see J. Organometal. Chem., 130(1977)173-301.

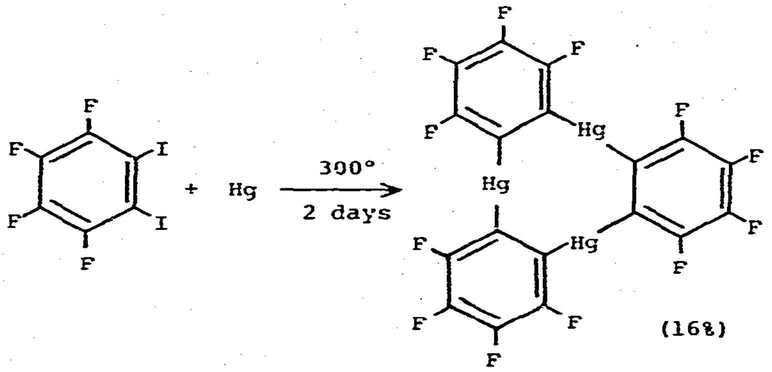
1. REVIEWS AND BOOKS

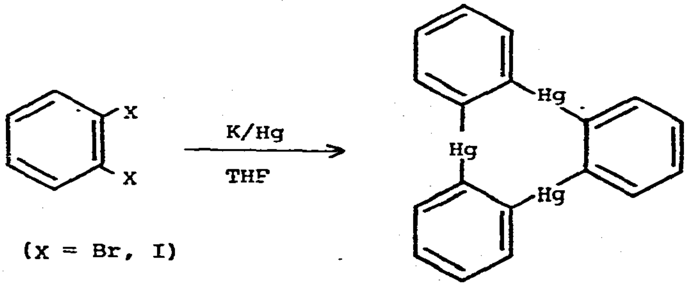
An excellent review of the applications of organomercury compounds in organic synthesis by R. C. Larock has been published in the first volume of the newly founded "Journal of Organometallic Chemistry Library" (1). Other reviews have covered the following topics:

- the polarography of organomercury compounds (2)
- reactions of organomercurials with organic halides, with the emphasis on questions of mechanism (3).

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

Elemental mercury has often served in the preparation of organomercurials. A new example of such a reaction brings a synthesis of a perfluorinated ortho-phenylene-mercury compound as well as of the fluorine-free analog (4):

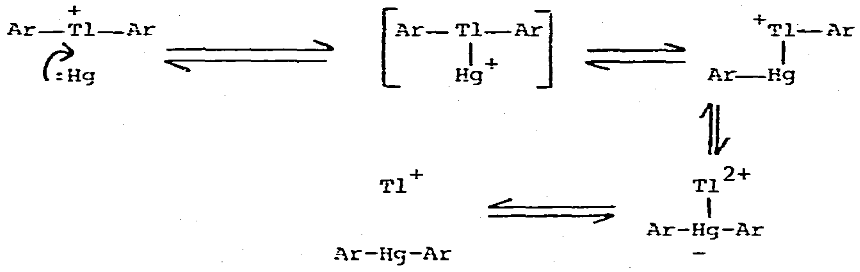




The kinetics of metal displacement in diarylthallium chlorides by elemental mercury have been studied by Reutov and his coworkers in DMF solution by a polarographic technique (5,6):

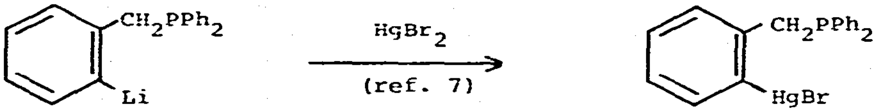
$$Ar_2TlCl + Hg \longrightarrow Ar_2Hg + TlCl$$

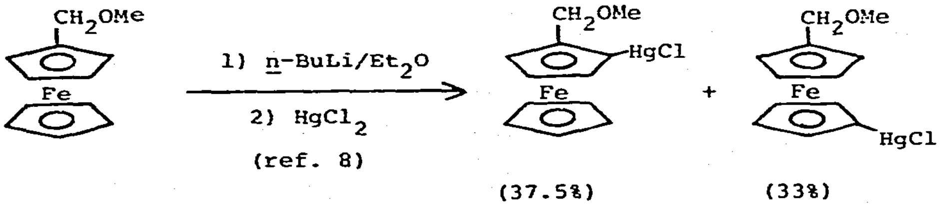
Electron-donating substituents in the aryl groups accelerated the process, while electron-withdrawing substituents had the opposite effect ($\rho = -2.83$). Such reactions also were studied in other solvents (pyridine, ethylene diamine, DMSO). A mechanism of the type shown below was proposed.



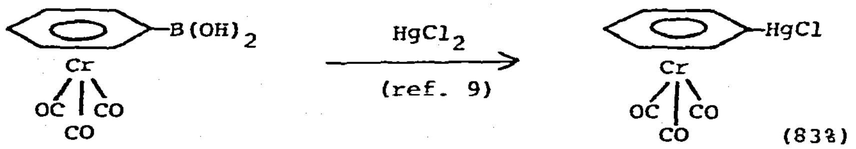
More useful in organomercurial preparation are reactions of organic derivatives of other metals with mercuric halides. Some new examples may be cited:

Organolithium reagents:



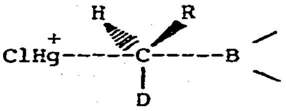


Organoboron Compounds:



$$\underline{\text{erythro}}\text{-}(\mathrm{Me_3CCHDCHD})_3\mathrm{B} \xrightarrow[\text{2) NaCl (ref. 10)}]{\text{1) Hg(OAc)}_2} \underline{\text{threo}}\text{-}\mathrm{Me_3CCHDCHDHgCl}$$

A similar reaction carried out with the threo isomer of the borane gave the erythro-alkylmercuric chloride. Thus the cleavage of the B-C bond in these compounds by mercuric acetate proceeds with inversion of configuration (10). Back-side attack by the electrophile on the B-C bond *via* a transition state such as 1 was suggested.



1

Organothallium compounds:

$$\mathrm{Ph_2TlX} + \mathrm{HgX_2} \xrightarrow[\text{(ref. 11)}]{} \mathrm{PhHgX} + \mathrm{PhTlX_2}$$

(X = halide, pseudohalide)

Organosilicon compounds:

$$\mathrm{PhSiX_3} + \mathrm{HgY_2} \xrightarrow[\text{(ref. 12)}]{} \mathrm{PhHgY} + \mathrm{SiX_3Y}$$

(X = F, OAc, OMe, OEt, Cl; Y = OAc, Cl)

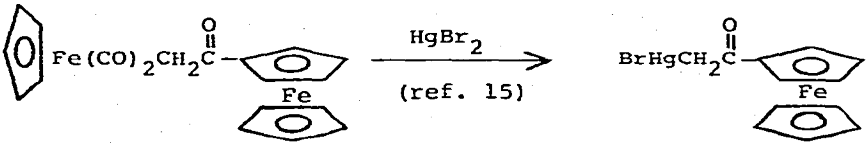
Organo-transition metal derivatives:

Mercuric halides and other Hg(II) compounds also cleave the C-M σ bonds of organo-transition metal derivatives. Such reactions, however, seldom have synthetic value since the organomercurials thus formed in most cases are more easily prepared by other routes.

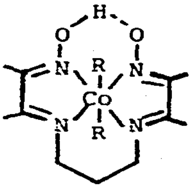
Nevertheless, we give new examples of such reactions since they are of interest from other points of view.

$$\underline{\text{trans}}\text{-PhCH=CHAuPPh}_3 \xrightarrow[\text{(ref. 13)}]{\text{HgBr}_2} \underline{\text{trans}}\text{-PhCH=CHHgBr}$$

$$(C_6F_5)_4Zr \xrightarrow[\text{(ref. 14)}]{\text{HgCl}_2} (C_6F_5)_2Hg \quad (89\%)$$



The transfer of σ-alkyl substituents from organocobalt complexes to Hg^{2+} or RHg^+ continues to be of interest and a number of preparative, kinetic and stereochemical studies on this subject have been reported in 1976 (16-22). Most of this work was concerned with alkyl- and alkenylcobaloxime systems, but other organocobalt complexes, e.g., 2, 3 and 4 (17) and 5 (18), were examined as well. These dialkylcobalt complexes were of interest in that products of type R_2Hg were formed.



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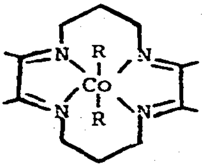
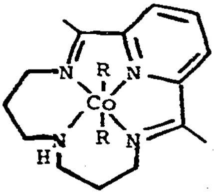


3

(R = CH_3)



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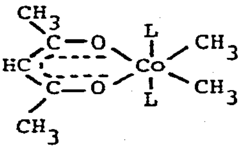


5

(L = $PPhMe_2$)

In another investigation, the kinetics and mechanism of alkyl transfer from $(H_2O)_5CrR^{2+}$ cations (R = Me, Et, n-Pr, CH_2CMe_3, $CHMe_2$, CH_2Cl, CH_2Br, CF_3, $CH_2C_6H_4Z$-p, with Z = H, Me, CN, CF_3, Br) to Hg^{2+} were studied (23). This process is believed to follow a bimolecular, electrophilic substitution mechanism.

The redistribution of substituents between two different mercury compounds:

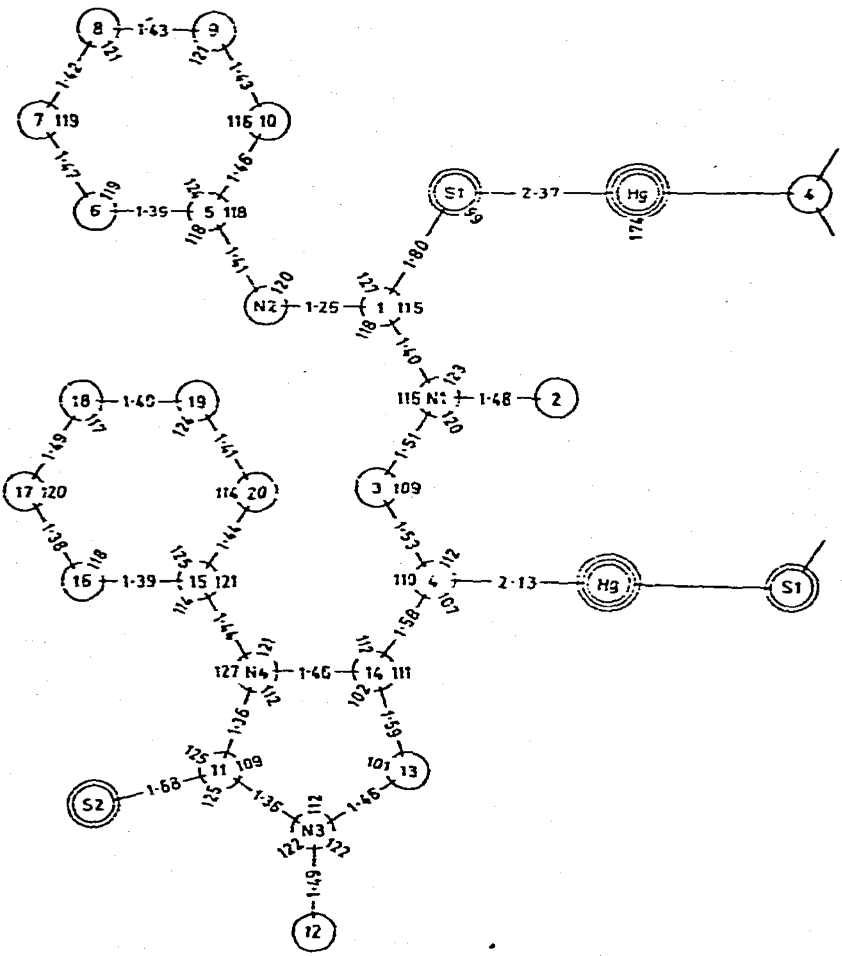


Figure 1. Molecular structure of 4,10-dimethyl-6,12-bis-(1-methyl-3-phenyl-2-thioxoimidazolidin-4-yl)-3,9-bis(phenyl-imino)-2,8-dithia-4,10-diaza-1,7-dimercuracyclododecane.
From: W. Ried, S.-W. Park and W. Schuckmann, Justus Liebigs Ann. Chem., 762 (1976).
Shown is one-half of the centrosymmetrical molecule.
Bond distances ±0.025Å; bond angles ±1.5°.

$$R_2Hg \quad + \quad R'_2Hg \rightleftharpoons 2\ RHgR'$$

$$R_2Hg \quad + \quad HgX_2 \rightleftharpoons 2\ RHgX$$

plays an important role in synthetic organomercury chemistry and has been the subject of many mechanistic studies. One of the research groups active in this area has studied the kinetics of the reactions of diarylmercurials with $Hg(CN)_2$ and $Hg(C{\equiv}CPh)_2$ in DMF by a polarographic method (24).

$$Ar_2Hg \quad + \quad (PhC{\equiv}C)_2Hg \rightleftharpoons 2\ ArHgC{\equiv}CPh \qquad (\rho = -3.24)$$

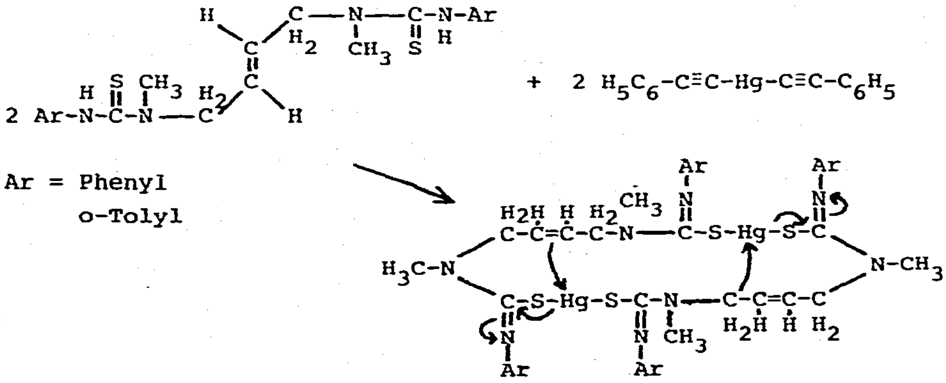
$$Ar_2Hg \quad + \quad Hg(CN)_2 \rightleftharpoons 2\ ArHgCN \qquad (\rho = -4.95)$$

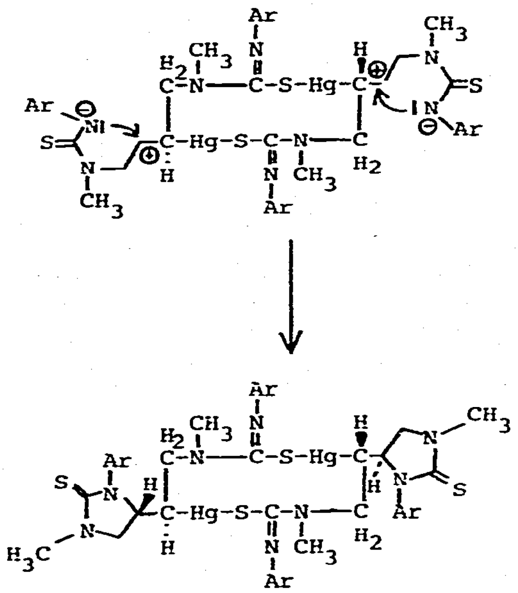
A preparative study has shown that cosymmetrization of two different arylmercuric acetates, each of which is capable of symmetrization under the reaction conditions, gives all three diarylmercury products (25):

$$ArHgOAc \quad + \quad Ar'HgOAc \xrightarrow[H_2O]{Na_4EDTA,\ n\text{-}BuNH_2} Ar_2Hg \quad + \quad Ar'_2Hg \quad + \quad ArHgAr'$$

As long as at least one of the two arylmercuric acetates symmetrizes, the unsymmetrical compound is formed.

A novel formation of a mercury-carbon bond is given in the reaction of bis(phenylethynyl)mercury shown below. The structure of the product was confirmed by an X-ray crystal structure determination (Fig. 1) (26).





The formation of methylmercury(II) species in the environment is an active area of research. In a new contribution, Japanese workers have found that mercuric sulfide is methylated slowly by aqueous acetic acid to give soluble CH_3Hg^+ species when it is irradiated with a blacklight lamp (27). The following steps were suggested to occur in this process:

1) formation of charge carriers:

$$HgS \xrightarrow{h\nu} \text{hole} + e^-$$

2) solubilization by hole-trapping:

$$\begin{tikzcd} HgS + 2\ \text{holes} \arrow[r] & Hg^{2+} + S \arrow[d, "OAc^-"] \\ & Hg(OAc)_2 \end{tikzcd}$$

3) photopolymerization of S atoms:

$$x\ S \xrightarrow{h\nu} S_x$$

4) decarboxylation, photosensitized by "photosulfur":

$$Hg(O_2CCH_3)_2 \xrightarrow[S_x]{h\nu} CH_3HgO_2CCH_3 + CO_2$$

3. USE OF ORGANOMERCURY COMPOUNDS IN SYNTHESIS

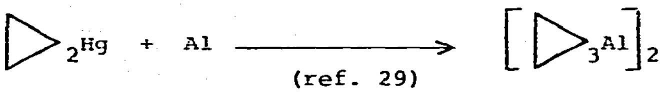
A. Synthesis of Organometallic Compounds

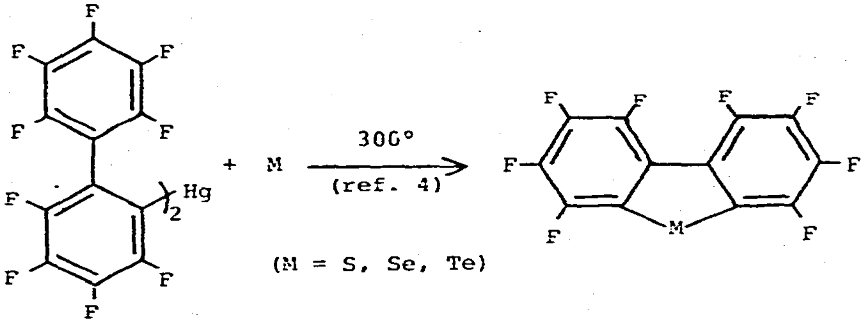
The reaction of R_2Hg compounds with metals and metalloids is a general route to organometallic and organometalloidal compounds which finds synthetic application, especially of organic derivatives of Main Groups I, II and III. Deacon and Vince have provided a very novel and interesting application of this old reaction in their synthesis of a σ-bonded perfluoro-organoytterbium compound (28):

$$(C_6F_5)_2Hg \quad + \quad Yb \quad \xrightarrow{\text{THF, } 25°} \quad (C_6F_5)_2Yb\cdot 4THF \quad + \quad Hg$$

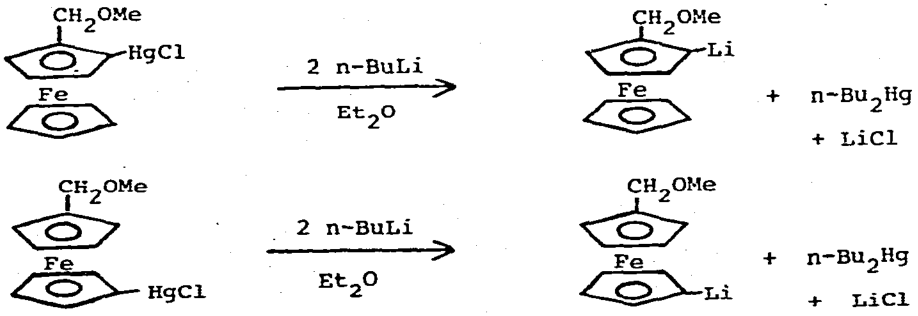
This is a reaction of some importance, especially if it is applicable to the synthesis of other C_6F_5 derivatives of the lanthanide and possibly even the actinide elements.

Also of interest are the following reactions:



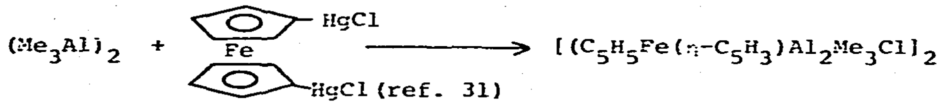


The Hg/Li transmetalation reaction has again been used to advantage in the ferrocene area (8):



Two examples of the use of organomercurials in the synthesis of Group III organometallics were recorded in 1976:

$$\mathrm{Me_2BCl} + \mathrm{Ph_2Hg} \xrightarrow[\text{(ref. 30)}]{\text{20°, sealed tube}} \underset{(37\%)}{\mathrm{Me_2BPh}} + \mathrm{PhHgCl}$$



An X-ray diffraction study of the product established the unusual structure shown in Figure 1a, which is that of a rearranged dimer of $(\eta\text{-}Me_2AlC_5H_4)Fe(\eta\text{-}MeClAlC_5H_5)$. (31).

Organomercurials have found application in organotin syntheses (32, 33):

$$\mathrm{ArHgOAc} + \mathrm{SnCl_2} \longrightarrow \mathrm{Ar_2SnCl_2}$$

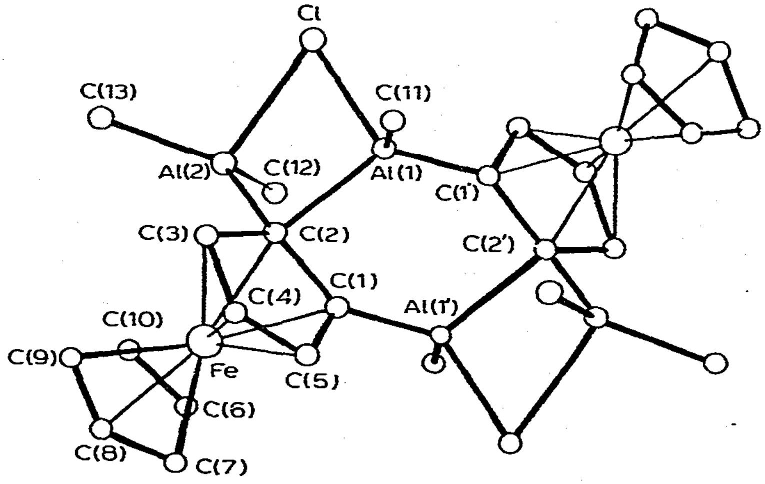
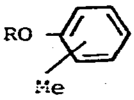


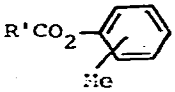
Figure 1a. Molecular structure of $[C_5H_5Fe(\eta\text{-}C_5H_3)Al_2Me_3Cl]_2$. From J. L. Atwood and A. L. Shoemaker, J. Chem. Soc. Chem. Comm., 536 (1976).

(Ar =



with R = n-Pr, n-Bu, n-C_5H_{11}, lauryl, cetyl for o, m, and p-methyl compounds

=



with R' = $CH_3(CH_2)_n$–, with n= 2, 6, 12, 14)

Organomercurials have attained particular importance in the synthesis of organo-transition metal compounds in substitution and oxidative addition processes. The equations below summarize the new advances in this area.

$$\mathrm{Me_2Hg} \;+\; \mathrm{WCl_6} \xrightarrow[\text{(ref. 34)}]{\mathrm{CH_2Cl_2},\ -45°} \mathrm{MeWCl_5} \;+\; \mathrm{MeHgCl}$$

$$\mathrm{Me_2Hg} \;+\; \mathrm{WOCl_4} \xrightarrow[\text{(ref. 34)}]{\mathrm{CH_2Cl_2/pentane},\ -80°} \mathrm{MeWOCl_3} \;+\; \mathrm{MeHgCl}$$

$$\mathrm{Ru(CO)_2L_2Cl_2} \;+\; \mathrm{R_2Hg} \xrightarrow[\text{(ref. 35)}]{\text{acetone}} \mathrm{Ru(CO)_2L_2ClR}$$

(L = PMe_2Ph, $PMePh_2$;
R = Me, Et, Ph;
all-trans and all-cis isomers)

$$[\mathrm{PtCl_2(AsPh_3)_2}] \;+\; [\mathrm{(CF_3)_2NO}]_2\mathrm{Hg} \xrightarrow[\text{(ref. 36)}]{} [\mathrm{Pt(ON(CF_3)_2)_2(AsPh_3)_2}]$$

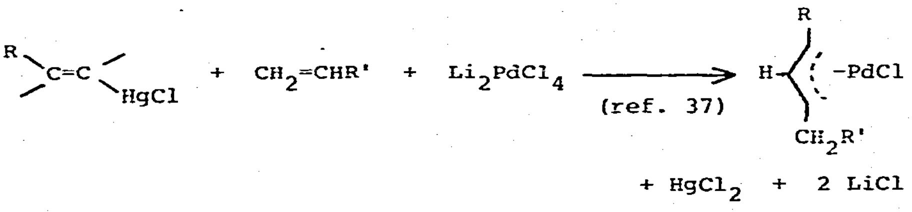
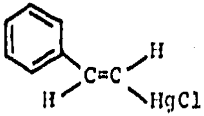
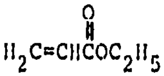
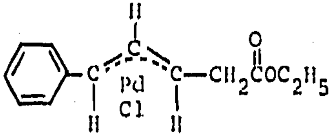
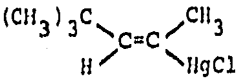
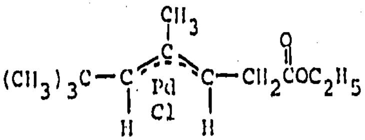
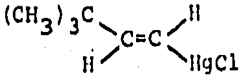
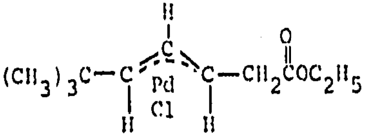
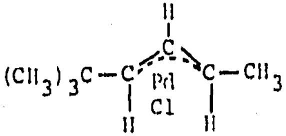
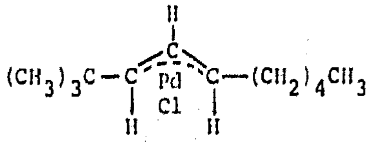
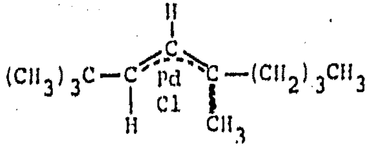
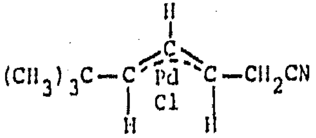
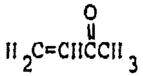
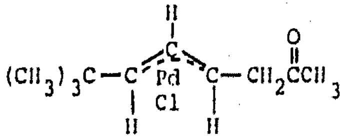
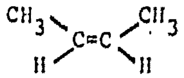
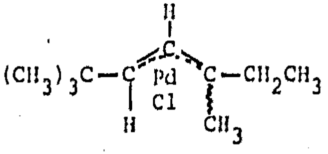
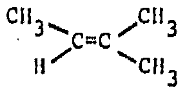
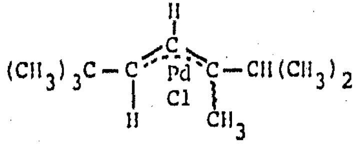


Table 1 gives specific examples of the application of this reaction. This procedure permits control of the position of the

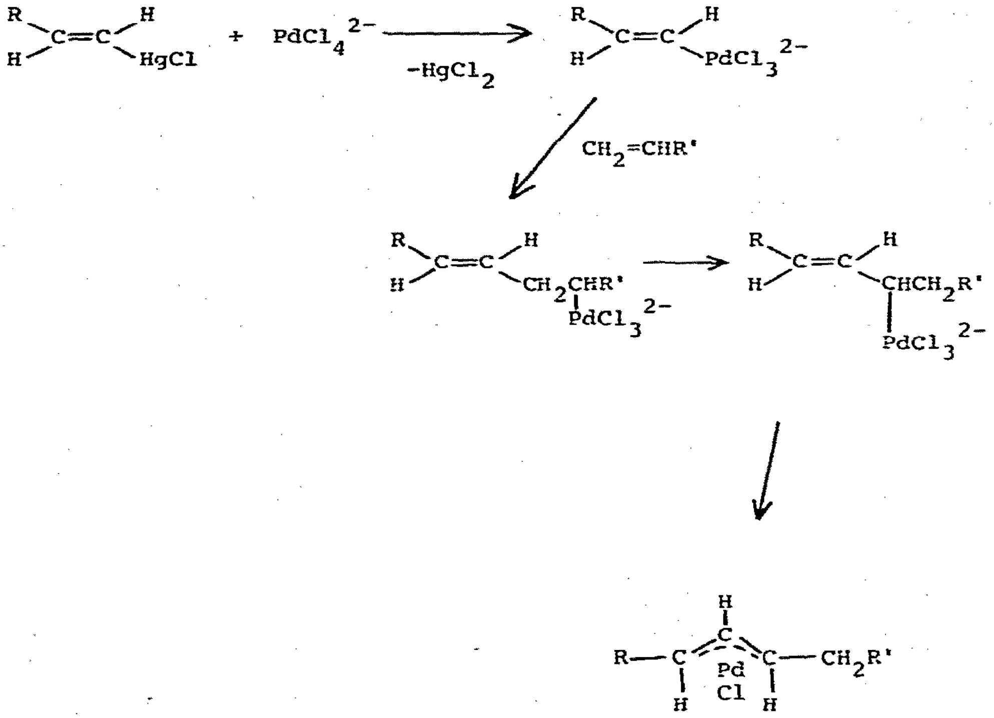
(Continued on p. 166)

TABLE 1. Synthesis of π-Allylpalladium Compounds by the Organomercury Route. From R.C. Larock and M.A. Mitchell, J. Amer. Chem. Soc., 98 (1976) 6718.

Vinylmercurial	Olefin	π-Allylpalladium compound	% yield
			crude (recryst.)
	 $H_2C{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5$		100 (58)
			97 (83)
			90 (82)
	$H_2C{=}CH_2$		92

$H_2C{=}CH(CH_2)_3CH_3$		67 (63)
		
$H_2C{=}CHCN$		87 (71)
 $H_2C{=}CH\overset{\overset{O}{\|}}{C}CH_3$		100 (67)
		59 (37)
		19 (7)

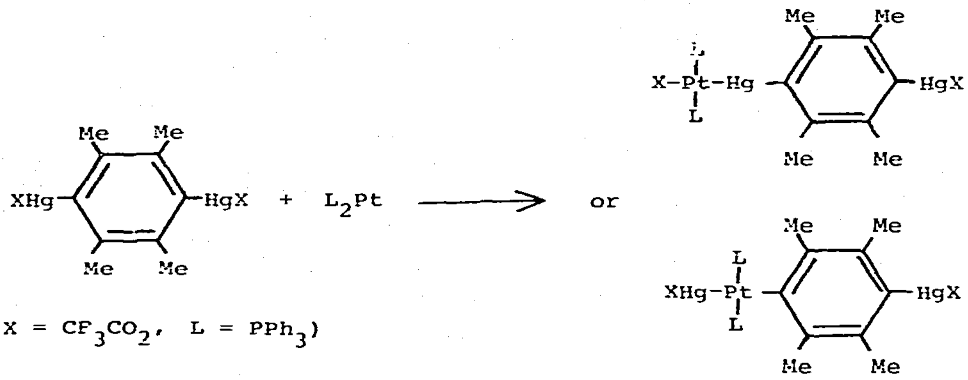
π-allyl system. A mechanism involving vinyl group transfer from mercury to palladium, followed by palladium hydride rearrangement, was suggested:



$$\mathrm{Pd(PPh_3)_4} + \mathrm{ClHgCH_2CN} \xrightarrow[\text{(ref. 38)}]{\text{THF, 40°}} \mathrm{(Ph_3P)_2PdCl(CH_2CN)} + \mathrm{Hg} + 2\ \mathrm{PPh_3}$$

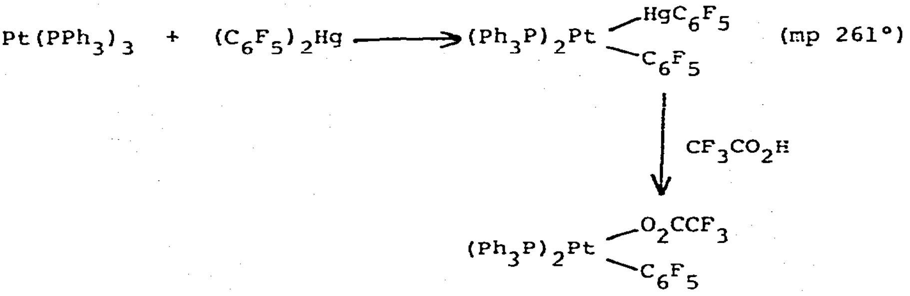
(but $Hg(CH_2CN)_2$ did not react in this manner, even under more drastic conditions).

Such oxidative additions of organomercurials to Pt(O) and Pd(O) had been reported earlier by Russian workers and are summarized in the 1974 and 1975 Annual Surveys. A further paper by the Russian group (39) brings more information on the subject:



(X = CF_3CO_2, L = PPh_3)

In the case of $Pt(Ph_3P)_2$, reaction with mercurated durene gave a Pt-Hg product which was not stable. Not only do steric factors play a role in stabilizing Pt-Hg bonds, but also electronic effects, as experiments with perfluorinated mercurials showed.



$$Pt(PPh_3)_3 + (C_6F_5)_2Hg \longrightarrow (Ph_3P)_2Pt(HgC_6F_5)(C_6F_5) \text{ (mp 261°)} \xrightarrow{CF_3CO_2H} (Ph_3P)_2Pt(O_2CCF_3)(C_6F_5)$$

In this example, the high melting point of the Pt-Hg product is indicative of its stability. Also, the compound $(Ph_3P)_2Pt(CF_3)$-$(HgCF_3)$ can be heated in refluxing xylene for many hours without decomposition.

In the absence of special steric or electronic effects, the Pt-Hg bonded compounds usually extrude mercury under the reaction conditions, forming a Pt-C bond:

$$R\text{-}Hg\text{-}R' + L_nPt \longrightarrow RHgPt(L)_2(R') \longrightarrow L_2PtRR' + Hg$$

This general process provides a useful route to σ-alkyl, alkenyl and aryl-platinum derivatives.

Dibenzylideneacetone-platinum and palladium complexes also are reactive toward organomercurials, but in order to obtain a stable product, an auxiliary ligand must be added:

$$Pd_2(DBA)_3\cdot C_6H_6^{*} + p\text{-}CH_3C_6H_4HgCl + 1,10\text{-phen} \longrightarrow p\text{-}CH_3C_6H_4PdCl(1,10\text{-phen}) + Hg$$

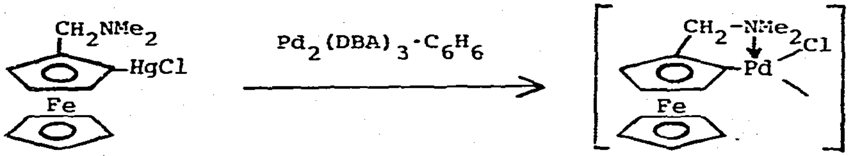
---

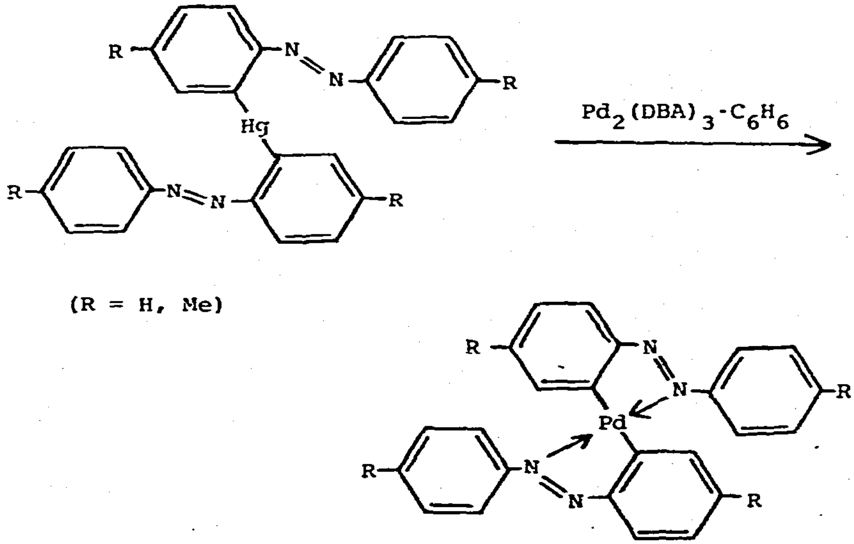
* DBA = dibenzylideneacetone

The reaction which occurs in the absence of the auxiliary ligand is illustrated for diphenylmercury:

$$Pd(DBA)_2 + Ph_2Hg \longrightarrow Ph\text{-}Ph + Pd + Hg + 2\ DBA$$

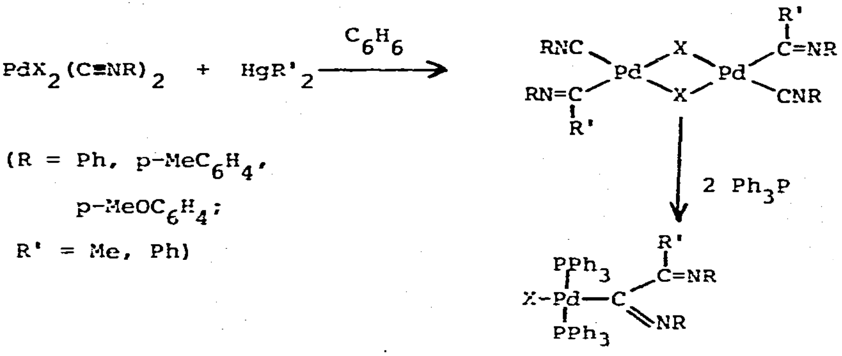
Such reactions have been used to prepare novel chelate complexes (40):





(R = H, Me)

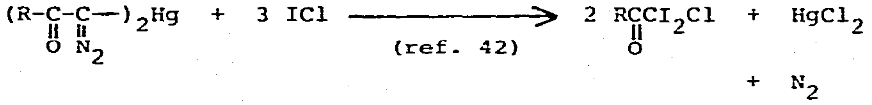
Finally, in this section, we note an example of coordinated ligand modification using organomercury reagents (41):



(R = Ph, p-MeC_6H_4,
p-$MeOC_6H_4$;
R' = Me, Ph)

B. Applications in Organic Synthesis

The simplest reaction of organomercurials which can be of synthetic utility is their cleavage by halogens and by protonic acids. (Studies relating to the mechanism of such processes will be covered in Section 6). Some new examples appeared in the 1976 literature:



$$(R\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{N_2}{\|}}{C}\text{—})_2Hg + 3\ ICl \xrightarrow[\text{(ref. 42)}]{} 2\ R\underset{\underset{O}{\|}}{C}CI_2Cl + HgCl_2 + N_2$$

(R = 1-adamantyl)

$$Hg(CN)_2 + 2\ I_2 \longrightarrow 2\ ICN + HgI_2$$

This reaction has been used for <u>in situ</u> ICN generation (43):

$$2\ RR'C(SEt)_2 + Hg(CN)_2 + I_2 \xrightarrow{\text{MeCN, } 60^\circ} 2\ RR'C(CN)SEt + HgI_2 + EtSSEt$$

Of special interest are the brominolysis and iodinolysis of mercurated nucleotides and polynucleotides using N-bromosuccinimide and molecular iodine to give the respective halogenated nucleotides and polynucleotides (44). (For the preparation of such mercurated nucleotides and polynucleotides, see Section 5). The reaction of these mercurated nucleotides with $NaBT_4$ gave tritiated products (44). In another isotopic synthesis, $CH_2CH^{36}Cl$ was obtained as shown below (45):

$$HgCl_2 + HC{\equiv}CH + H^{36}Cl_{aq} \longrightarrow ClHgCH{=}CH^{36}Cl$$

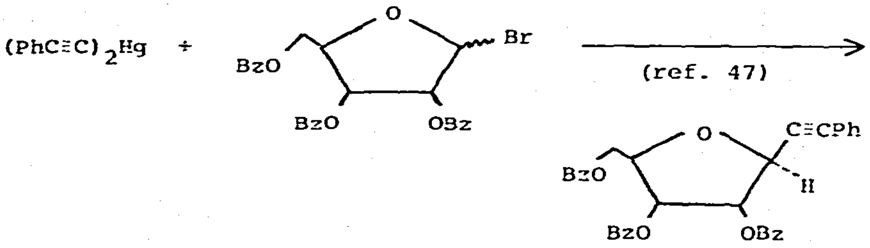
$$ClHgCH{=}CH^{36}Cl + 10\ \underline{M}\ HCl \longrightarrow HgCl_2 + CH_2{=}CH^{36}Cl$$

Alkylation of organic halides with organomercurials also is a reaction of some utility:

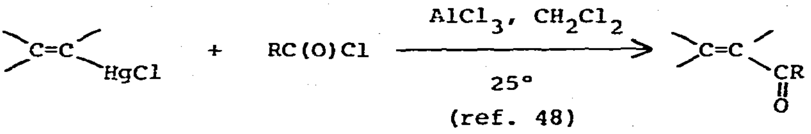
$$2\ HC(CN)_3 + HgO \xrightarrow{Et_2O} Hg[C(CN)_3]_2 + H_2O$$

$$Hg[C(CN)_3]_2 + 2\ PhCH_2Cl \xrightarrow[\text{(ref. 46)}]{DMSO} 2\ PhCH_2C(CN)_3 + HgCl_2$$

(Column chromatography (Al_2O_3) of the reaction mixture gave a mixture of $PhCH_2CH(CN)_2$ and $PhCH_2CH(CN)C(O)NH_2$).



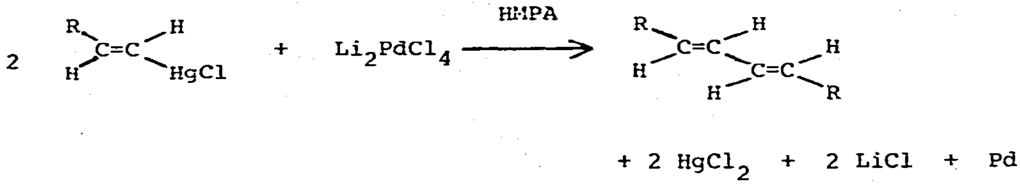
(+ minor amount of the other isomer)



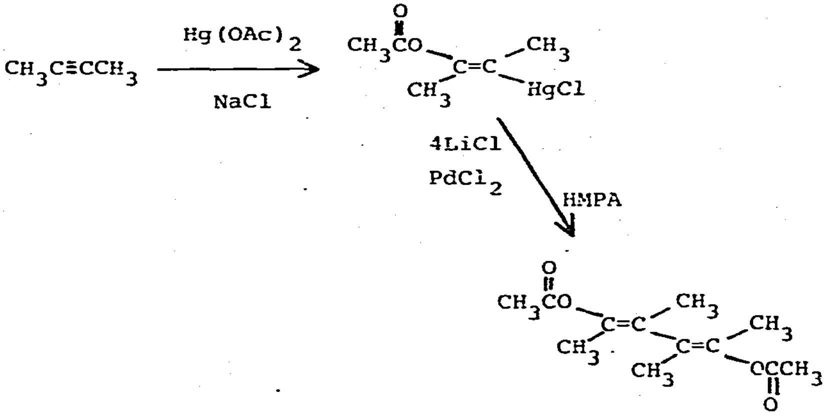
Specific examples reported by Larock of this useful synthesis of α, β-unsaturated ketones based on the acetylene hydroboration/mercurideboronation sequence are given in Table 2.

Substituent transfer from mercury to palladium with subsequent reactions of the organopalladium intermediate formed to give organic products is a useful application of organomercurials to organic synthesis which was developed by Heck a few years ago. This reaction has received continued study since then, and a number of further examples of such processes, some of them of promising synthetic utility, have been reported.

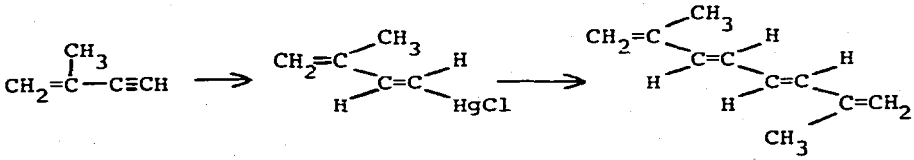
1) Coupling reactions (49).

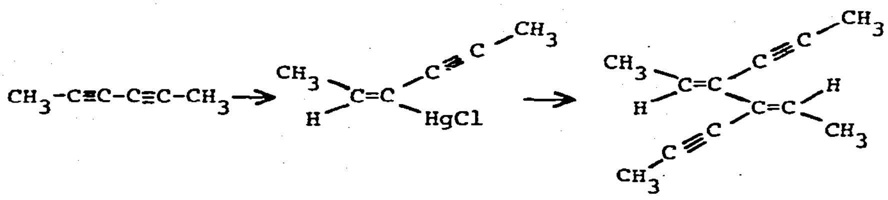


e.g.:



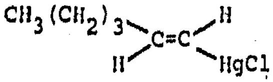
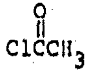
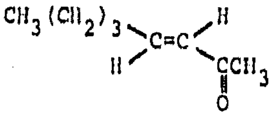
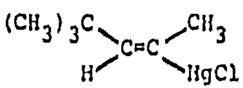
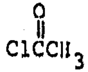
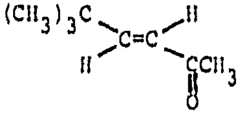
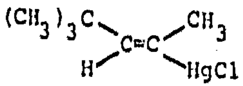
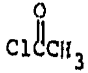
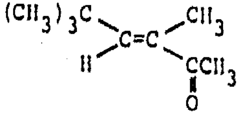
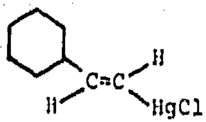
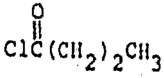
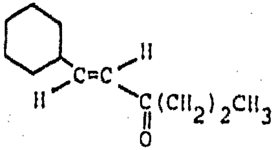
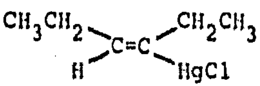
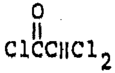
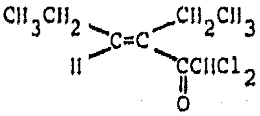
Similarly (via hydroboration/mercurideboronation/coupling):





(Continued on p. 174)

TABLE 2. Synthesis of α, β-Unsaturated Ketones from Vinylmercury Compounds. From R. C. Larock and J. C. Bernhardt, Tetrahedron Lett. (1976) 3097.

VINYLMERCURIAL	ACID CHLORIDE	KETONE	% YIELD
	 $\mathrm{Cl\overset{O}{\overset{\|}{C}}CH_3}$		97
	 $\mathrm{Cl\overset{O}{\overset{\|}{C}}CH_3}$		95
	 $\mathrm{Cl\overset{O}{\overset{\|}{C}}CH_3}$		99
	 $\mathrm{Cl\overset{O}{\overset{\|}{C}}(CH_2)_2CH_3}$		96
	 $\mathrm{Cl\overset{O}{\overset{\|}{C}}CHCl_2}$		89

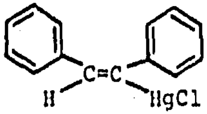
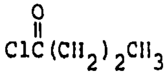
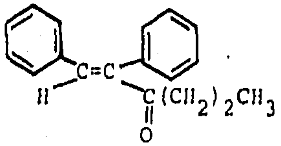
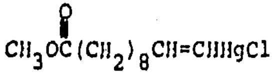
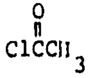
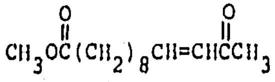
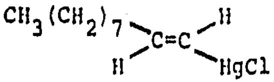
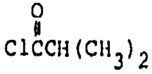
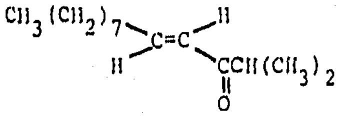
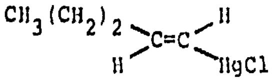
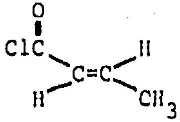
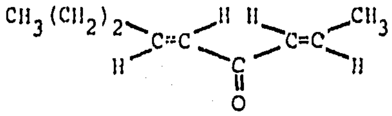
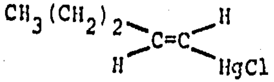
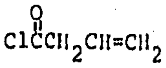
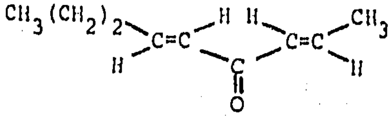
	 $Cl\overset{O}{C}(CH_2)_2CH_3$		72
 $CH_3O\overset{O}{C}(CH_2)_8CH{=}CHHgCl$	 $Cl\overset{O}{C}CH_3$	 $CH_3O\overset{O}{C}(CH_2)_8CH{=}CH\overset{O}{C}CH_3$	100
	 $Cl\overset{O}{C}CH(CH_3)_2$		97
			97
	 $Cl\overset{O}{C}CH_2CH{=}CH_2$		91

Table 3 gives further examples of this reaction. These are stoichiometric reactions, and since expensive palladium reagents are involved, a catalytic process would be preferable. Tetrakis-(triphenylphosphine)palladium(O)/LiCl catalyzes vinylmercuric chloride coupling in HMPA at 0°, but the yields and stereo-

TABLE 3. Syntheses of Dienes and Polyenes from Vinylmercurials. From R. C. Larock, J. Org. Chem., 41 (1976) 2241.

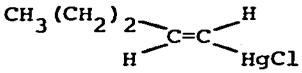
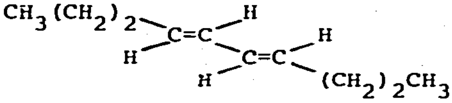
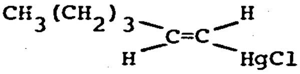
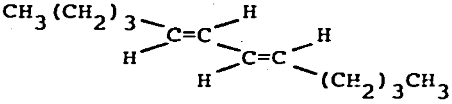
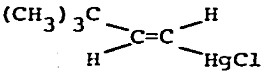
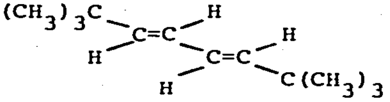
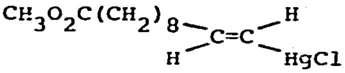
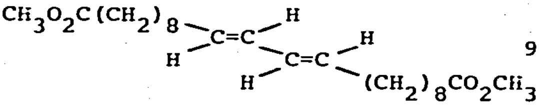
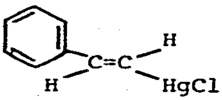
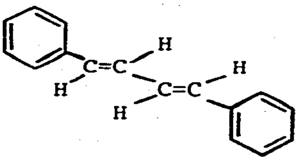
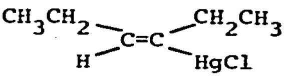
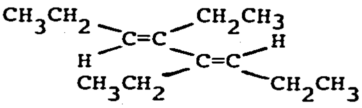
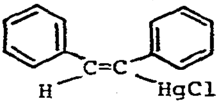
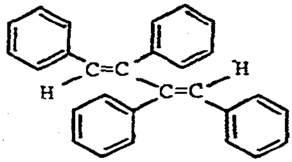
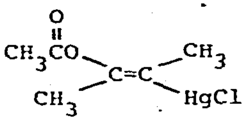
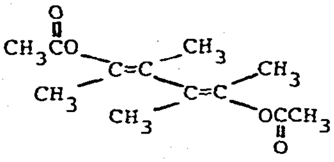
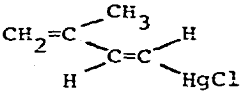
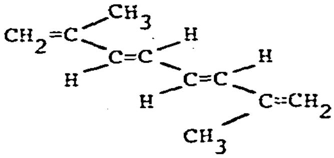
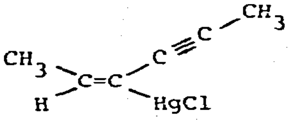
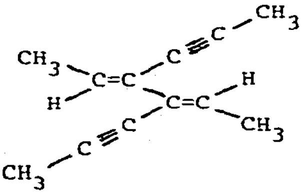
Organomercurial	Dimer	Yield, %
		98
		100
		96
		94
		100
		75

TABLE 3.

		100
		82
		95
		92

specificity are inferior to those obtained in the stoichiometric process (Table 4).

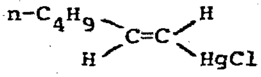
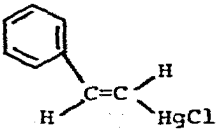
$$CH_2{=}CHCH_2HgI \xrightarrow[\substack{\text{HMPA} \\ (\text{ref. } 49)}]{Li_2PdCl_4} CH_2{=}CHCH_2CH_2CH{=}CH_2 \qquad (70\%)$$

$$PhCH_2HgCl \xrightarrow[\substack{\text{HMPA} \\ (\text{ref. } 49)}]{Li_2PdCl_4} \underset{(70\%)}{PhCH_2CH_2Ph} \qquad \text{(slow reaction)}$$

$$\mathrm{PhHgCl} \xrightarrow[\text{HMPA (ref. 49)}]{\mathrm{Li_2PdCl_4}} \underset{(87\%)}{\text{Ph-Ph}} \quad \text{(rapid reaction)}$$

$$\mathrm{Ph_2Hg} \xrightarrow[\text{HMPA (ref. 49)}]{\mathrm{Li_2PdCl_4}} \underset{(95\%)}{\text{Ph-Ph}}$$

Table 4: $(Ph_3P)_4$Pd-catalyzed[a] Coupling of Vinylmercurials. From R. C. Larock, J. org. Chem., 41 (1976) 2241.

		Diene yield, %		
Vinylmercuric chloride[b]	Lithium chloride[c]	trans, trans	cis,trans	Total
	–	42	2	44
	+	59	2	61
	–	46	2	48
	+	80		80

[a] 0.1 mmol catalyst. [b] 2.0 mmol. [c] Either 0 or 4 mmol.

Kretchmer and Glowinski have developed a more useful catalytic biaryl synthesis in which arylmercuric acetates and chlorides are heated at 115° in pyridine solution in the presence of above-stoichiometric amounts of copper powder and catalytic quantities of palladium(II) chloride (50). As Table 5 shows, this reaction is compatible with diverse functional groups, but some do interfere. Cross-coupling is not a selective process:

$$\begin{array}{c} \mathrm{C_6H_5HgOAc} \\ + \\ p\text{-}\mathrm{MeOC_6H_4HgOAc} \end{array} \xrightarrow[\mathrm{(PdCl_2)}]{\mathrm{Cu,\ C_5H_5N}} \begin{array}{ll} \mathrm{C_6H_5\text{-}C_6H_5} & (33\%) \\ p\text{-}\mathrm{MeOC_6H_4\text{-}C_6H_5} & (48\%) \\ p\text{-}\mathrm{MeOC_6H_4\text{-}C_6H_4OMe}\text{-}p & (19\%) \end{array}$$

TABLE 5. Coupling of Arylmercuric Salts with $PdCl_2$ and Copper in Pyridine. From R. A. Kretchmer and R. Glowinski, J. Org. Chem., 41 (1976) 2661.

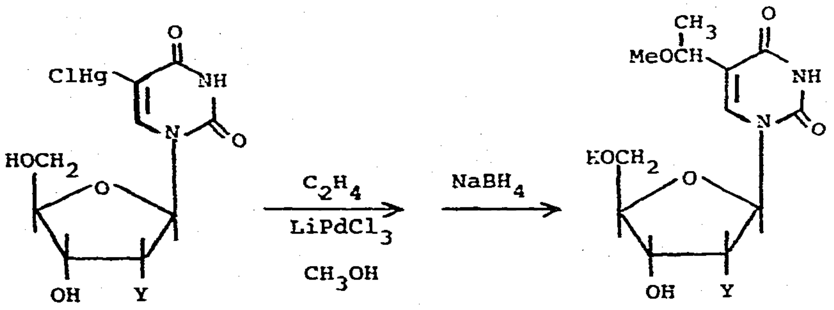
Arylmercuric salt	Coupling product	Yield %[b]
Phenylmercuric acetate	Biphenyl	86
2-Methoxyphenylmercuric acetate	2,2'-Dimethoxybiphenyl	84
4-Methoxyphenylmercuric acetate	4,4'-Dimethoxybiphenyl	90
4-Aminophenylmercuric acetate	Benzidine	76
4-Acetamidophenylmercuric acetate	4,4'-Diacetamidobiphenyl	69
4-Chlorophenylmercuric acetate	4,4'-Dichlorobiphenyl	62[c]
2-Chloromercurifuran	2,2'-Bifuran	86
2-Chloromercurithiophene	2,2'-Bithiophene	95
1-Chloromercurinaphthalene	1,1'-Binaphthalene	47
4-Chloromercuribenzoic acid	None	0
4-Chloromercuriphenol	None	0
Mesitylmercuric acetate	None	0

[a] The reactions were carried out at reflux under a nitrogen atmosphere for a period of 22h unless otherwise specified.

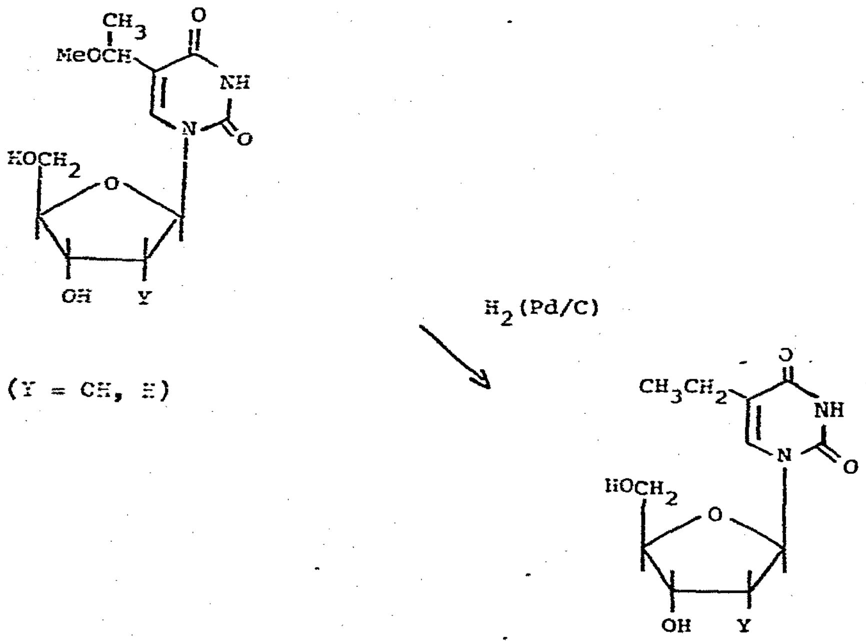
[b] Isolated yield. [c] A reaction period of 5 h was used.

2) Other processes

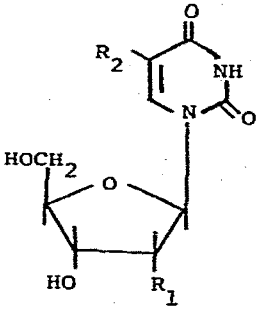
a) Synthesis of C-5 substituted pyrimidine nucleosides (51)



(Y = OH, H)



Using this general method with olefins other than ethylene permitted the preparation of other 5-alkyluridines:



R_1 = OH; R_2 = CH_2CH_3

R_1 = H; R_2 = CH_2CH_3

R_1 = H; R_2 = $CH_2CH_2CH_2CHOHCH_2OH$

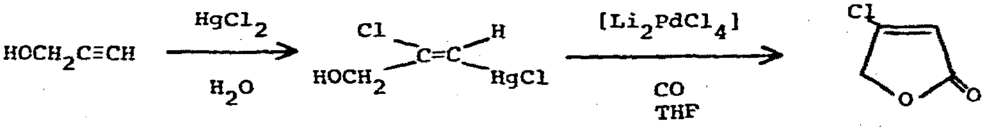
R_1 = OH; R_2 = $CH{=}CHCO_2CH_3$

R_1 = OH; R_2 = $CH_2CH{=}CH_2$

The allyl compound was obtained by Li_2PdCl_4-catalyzed coupling of the mercury derivative and allyl chloride.

b) A $\Delta^{\alpha,\beta}$ -butenolide synthesis (52)

Larock has combined a hydroxymethylacetylene chloromercuration/Pd-catalyzed carbonylation sequence into a very nice synthesis of $\Delta^{\alpha,\beta}$-butenolides:



In addition to this stoichiometric process, examples of which are given in Table 6, a process catalytic in PdCl_2 using two equivalents of copper(II) chloride as reoxidizer and benzene as solvent was developed.

c) Carboxylation of aromatic compounds (53):

$$\underset{\text{1 part}}{\text{PhHgOAc}} + \underset{\text{1 part}}{\text{Pd(OAc)}_2} + \underset{\text{10 parts}}{\text{NaOAc}} \xrightarrow[\text{100°, 5 hr}]{\text{HOAc/Ac}_2\text{O}}$$

$$\text{PhCO}_2\text{H}\ \ (60\%) + \text{Ph-Ph}\ \ (1\%)$$

$$+ \text{PhOAc}\ \ (2\%)$$

d) Synthesis of dialkyl oxalates and dialkyl carbonates (54):

$$\text{AcOHgCO}_2\text{Me} + \text{PdCl}_2 \xrightarrow{\text{MeOH}} \text{MeO}_2\text{C-CO}_2\text{Me} + \text{Pd} + 2\ \text{HgCl}_2$$

$$\text{AcOHgCO}_2\text{Me} + 2\ \text{CuCl}_2 + \text{MeOH} \longrightarrow (\text{MeO})_2\text{CO} + 2\ \text{CuCl}$$

$$+ \text{HgCl}_2 + \text{MeCO}_2\text{H}$$

$\text{AcOHgCO}_2\text{Me}$ also decomposes into dimethyl carbonate (86% yield) in methanol solution in the presence of sodium methoxide.

Nefedov et al. (55) have reported further work on the carbonylation of amines in the presence of mercuric acetate:

$$4\ \text{RR'NH} + \text{CO} + \text{Hg(OAc)}_2 \xrightarrow{\text{50-110°}} 2\ (\text{RR'N})_2\text{CO} + \text{Hg}$$

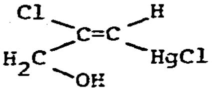
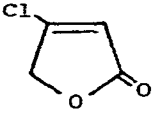
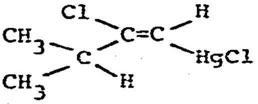
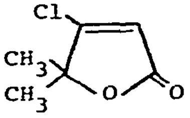
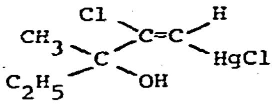
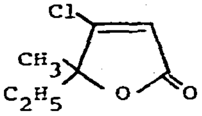
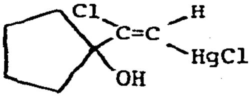
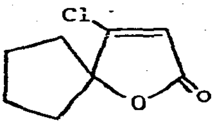
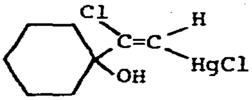
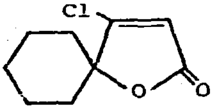
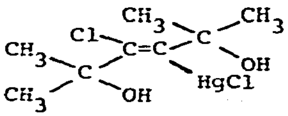
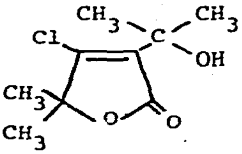
$$+ 2\ \text{HOAc} + \text{H}_2$$

The effects of various variables ($\text{p}K_a$ of the amine, reaction time and temperature, solvent) were studied and the following mechanism was proposed:

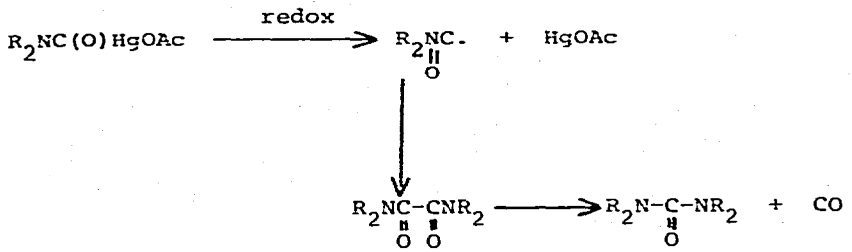
$$2\ \text{R}_2\text{NH} + \text{Hg(OAc)}_2 \rightleftharpoons (\text{R}_2\text{NH})_2\cdot\text{Hg(OAc)}_2 \qquad \text{(CT complex)}$$

$$(\text{R}_2\text{NH})_2\cdot\text{Hg(OAc)}_2 + \text{CO} \longrightarrow \text{R}_2\text{NC(O)HgOAc} + \text{R}_2\text{NH}_2^{+}\ \text{OAc}^{-}$$

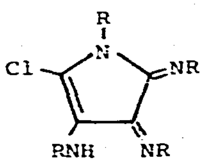
TABLE 6. Synthesis of β-Chloro-$\Delta^{\alpha,\beta}$-butenolides by the Organomercury Route. From R. C. Larock and B. Riefling, Tetrahedron Lett. (1976) 4661.

Vinylmercurial	Butenolide	% Yield
		(96)
		100(86)
		91
		99
		100(92)
		94

It was noted that when aniline is carbonylated in the presence of mercuric chloride, the reaction does not proceed past the formation of PhNHC(O)HgCl which was characterized by IR spectro-



scopy. Also of interest is the formation of low molecular weight and cyclic oligomers, e.g., 6, 7 and 8, on reaction of bulky isonitriles such as 2,6-xylylisonitrile, with mercuric chloride in dry, refluxing THF in the presence of ethanol or diphenylamine (56). With unhindered isonitriles, e.g., benzylisonitrile, the reaction with $HgCl_2$ in THF gave polymeric



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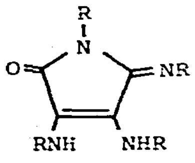

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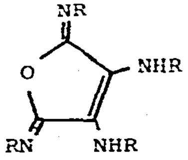

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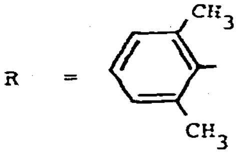


products of low (700-800) molecular weight. Mercury-carbon bonded intermediates, $(RN{\equiv}C{\cdot}HgCl_2)_2$ and $RN{=}C(Cl)HgCl$, are involved in these reactions.

Of possible utility in organic synthesis is a mild, mercury-based reduction of tosylhydrazones (57):

$$Ar(R)C{=}NNHSO_2C_6H_4Me\text{-}p \xrightarrow[MeOH]{Hg(OAc)_2} (Ar(R)C{=}\underset{|}{N}NSO_2C_6H_4Me\text{-}p)_2Hg \quad (87\text{-}98\%)$$

$$(Ar(R)C{=}\underset{|}{N}NSO_2C_6H_4Me\text{-}p)_2Hg \xrightarrow{NaBH_3CN} Ar(R)CHNHNHSO_2C_6H_4Me\text{-}p \quad (87\text{-}96\%)$$

In the examples given, Ar = Ph and p-MeC_6H_4 and R = Me, Et, Ph and $PhCH_2$.

New nitro compounds have been prepared by reactions of nitroalkylmercurials (58):

$$(O_2N)_3CCHRCH_2HgC(NO_2)_3 \;+\; CH_2O \xrightarrow{H_2O} (O_2N)_2C(CH_2OH)_2$$

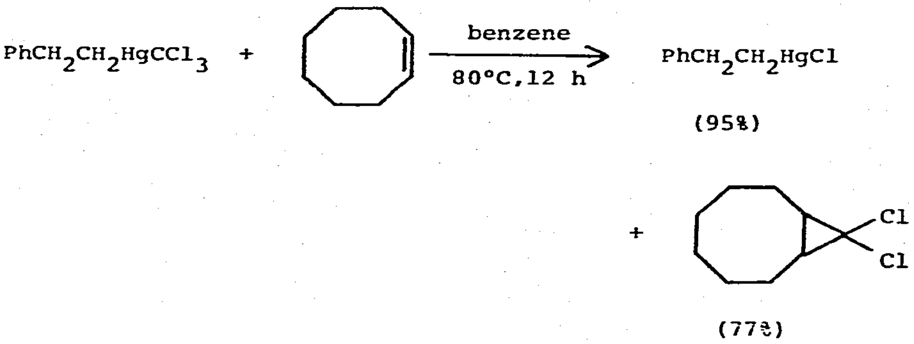
$$[(O_2N)_3C]_2Hg \;+\; CH_2O \xrightarrow{H_2O} (O_2N)_3CCCH_2OH$$

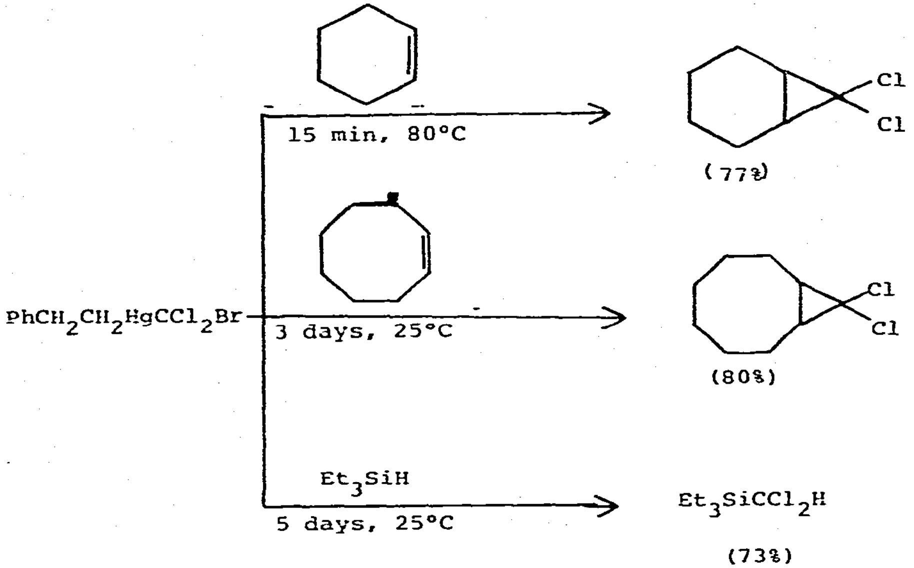
C. Halomethyl-Mercury Compounds

New alkyl(trihalomethyl)mercury compounds which are useful as room temperature sources of dihalocarbenes have been developed (59):

$$RHgCl \;+\; Me_3COK \xrightarrow{THF,\ -60°} \xrightarrow{CHX_3} RHgCX_3 \;+\; Me_3COH \;+\; KCl$$

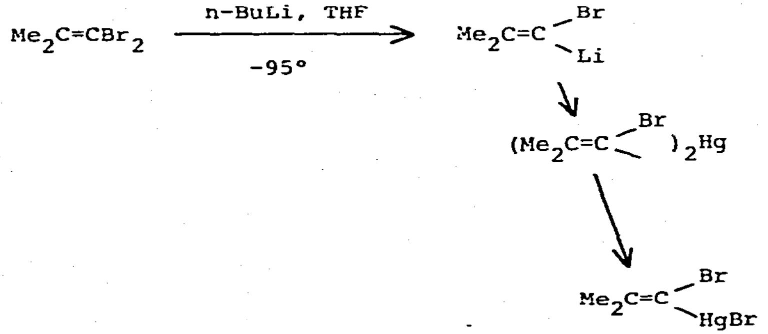
Prepared in this manner were $PhCH_2HgCCl_3$, $PhCH_2CH_2HgCCl_3$, $PhCH_2CH_2HgCCl_2Br$, $PhCH_2CH_2HgCBr_3$, cyclo-$C_6H_{11}HgCCl_3$, cyclo-$C_6H_{11}HgCCl_2Br$, cyclo-$C_6H_{11}HgCClBr_2$ and cyclo-$C_6H_{11}HgCBr_3$. Of these, the benzyl derivative was not a useful carbene reagent, decomposing at 80° with formation of elemental mercury in an apparently homolytic process. The others, however, were divalent carbon transfer agents, e.g.:





The cyclohexylmercurials, cyclo-$C_6H_{11}HgCCl_2Br$ and cyclo-$C_6H_{11}HgCClBr_2$, were especially effective in reactions with olefins and triethylsilane, at room temperature as well as at 80°. The preparative results are given in Table 7, and Table 8 presents a comparison of the relative reactivities of alkyl- and aryl-(trihalomethyl)mercurials as dihalocarbene sources. In spite of their apparent advantages, the alkyl(trihalomethyl)mercury reagents will probably remain unutilized in synthesis: they are more soluble and less stable, hence more difficult to isolate, than the $PhHgCX_3$ reagents; they appear to be subject to autoxidation, induced decomposition in the presence of oxygen-containing solvents such as acetone, and they exhibit poor stability on storage.

A new mercury reagent which is a useful source of the carbene $Me_2C{=}C{:}$ at 150° has been prepared (60):



(Continued on p. 194)

TABLE 7. Divalent Carbon Transfer Reactions of Cyclohexyl- and ß-Phenylethyl(trihalomethyl)mercury Compounds. From D. Seyferth, C. K. Haas and D. Dagani, J. Organometal. Chem., 104 (1976) 9.

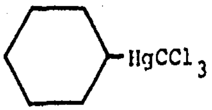
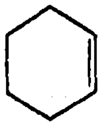
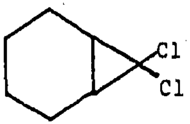
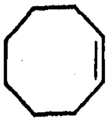
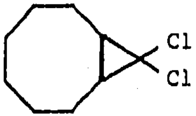
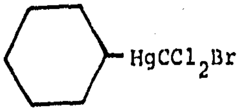
Carbenophile	Reaction conditions[a]		Product, (% Yield)		RHgX (% yield)
	Time	Temp. (°C)			
A. 					
	6.5 h	80		(92)	
	8 h	80		(90)	95
Et_3SiH	8 h	80	Et_3SiCCl_2H	(88)	97

TABLE 7. (contd.)

B. 

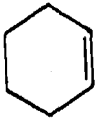
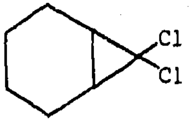
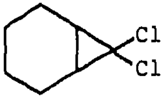
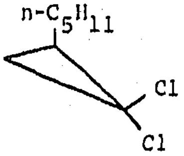
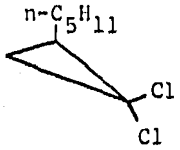
	6 min	80		(96)	95
	49 h	25		(95)	85
n-$C_5H_{11}CH{=}CH_2$	8 min	80		(76)	91
n-$C_5H_{11}CH{=}CH_2$	41 h	25		(85)	94

TABLE 7 (contd.)

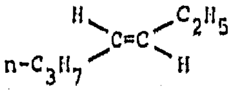
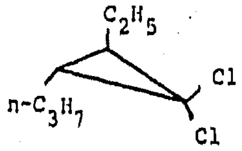
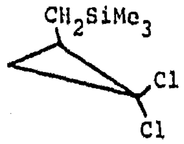
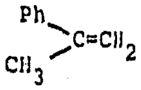
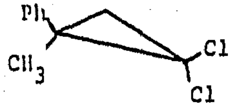
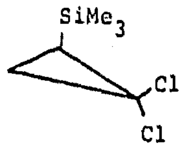
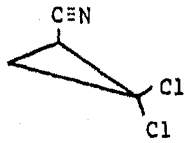
 $n\text{-}C_3H_7(H)C=C(H)C_2H_5$	50 h	25		(88)	80
$Me_3SiCH_2CH=CH_2$	46 h	25		(88)	93
 $Ph(CH_3)C=CH_2$	46 h	25		(84)	94
$Me_3SiCH=CH_2$	44 h	25		(68)	79
$CH_2=CHCN$	46 h	25		(45)	72

TABLE 7 (contd.)

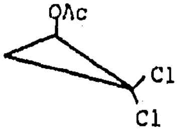
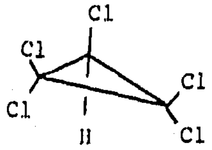
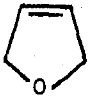
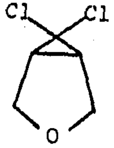
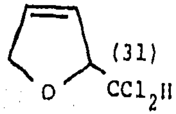
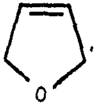
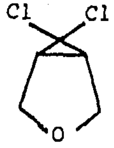
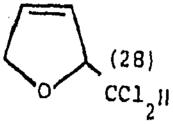
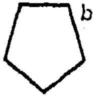
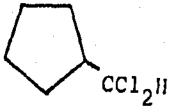
 $CH_3\overset{O}{\overset{\|}{C}}OCH\text{-}CH_2$	48 h	25		(81)	97
$CHCl{=}CCl_2$	48 h	25		(22)	92
	10 min	80	 (24) + 	(31)	84
	72 h	25	 (34) + 	(28)	88
 b	42 h	25		(35)	71

TABLE 7(contd.)

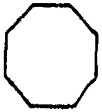
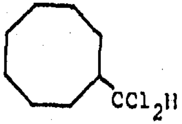
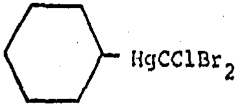
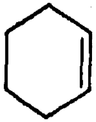
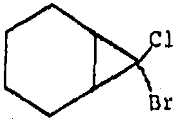
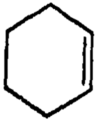
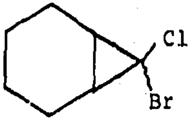
 [b]	48 h	25		(38)	90
Et_3SiH	50 h	25	Et_3SiCCl_2H	(80)	89
C. 					
	7 min	80		(85)	90
	72 h	25		(87)	91

TABLE 7. (contd.)

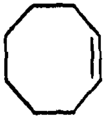
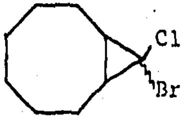
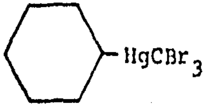
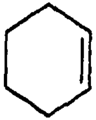
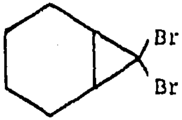
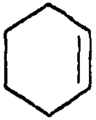
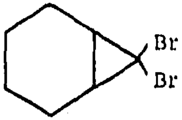
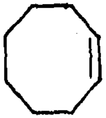
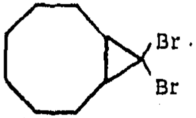
	72 h	25		(83)	90
Et_3SiH	72 h	25	$Et_3SiCClBrH$	(70)	90
D. 					
	10 min	80		(40)	90^c
	48 h	25		(50)	80^c
	48 h	25		(34)	80^c

TABLE 7 (contd.)

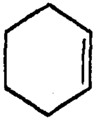
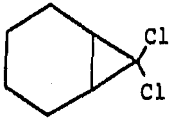
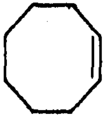
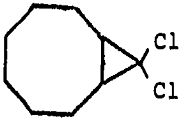
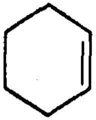
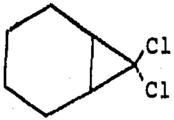
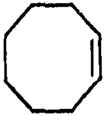
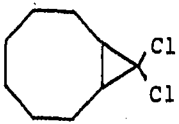
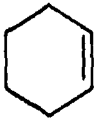
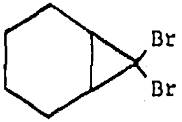
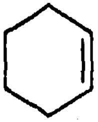
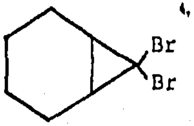
E. $PhCH_2CH_2HgCCl_3$					
	14 h	80		(65)	89
	12 h	80		(77)	95
F. $PhCH_2CH_2HgCCl_2Br$					
	15 min	80		(77)	91
	72 h	25		(80)	85
Et_3SiH	120 h	25	Et_3SiCCl_2H	(73)	72

TABLE 7 (contd.)

G. $PhCH_2CH_2HgCBr_3$

	96 h	25		(10)	
	20 min	30		(24)	42[c]

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[a] Three molar equivalents of carbenophile per equivalent of mercury reagent in benzene solution unless otherwise noted. [b] Cycloalkane used as solvent. [c] Impure material, grey in color.

TABLE 8. Comparison of the Reactivities of Alkyl- and Aryl-(trihalomethyl)mercury Compounds as Divalent Carbon Transfer Reagents. From D. Seyferth, C.K. Haas and D. Dagani, J. Organometal. Chem., 104 (1976) 9.

APPROXIMATE REACTION TIMES FOR CX_2 TRANSFER FROM $RHgCX_3$

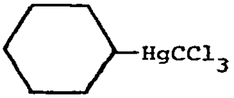
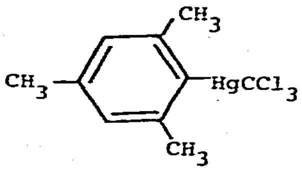
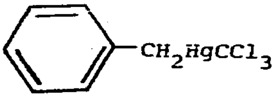
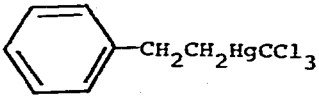
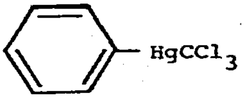
Mercurial	Time	
	Room Temp.	80°C
		8 h
		30 h
		rapid formation of Hg^0; no CCl_2
		12 h
		30-48 h

TABLE 8 (contd.)

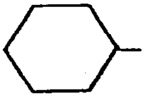
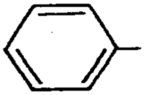
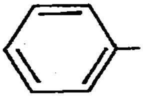
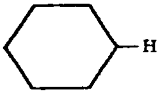
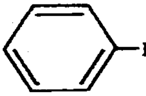
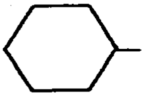
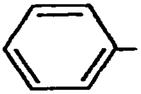
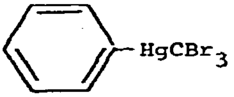
 $HgCCl_2Br$	2 d	<10 min
 $CH_2CH_2HgCCl_2Br$	3 d	<15 min
 $HgCCl_2Br$	18 d	2 h
 $HgCClBr_2$	3 d	<10 min
 $HgCClBr_2$	16 d	2 h
 $HgCBr_3$	2 d	<10 min
 $CH_2CH_2HgCBr_3$	4 d	<20 min

TABLE 8 (contd.)

	15 d	2 h

The transfer of $Me_2C{=}C{:}$ from this mercurial to olefins proceeded most cleanly and in highest yield when a 1:1 molar mixture of $Me_2C{=}C(Br)HgBr$ and diphenylmercury was used:

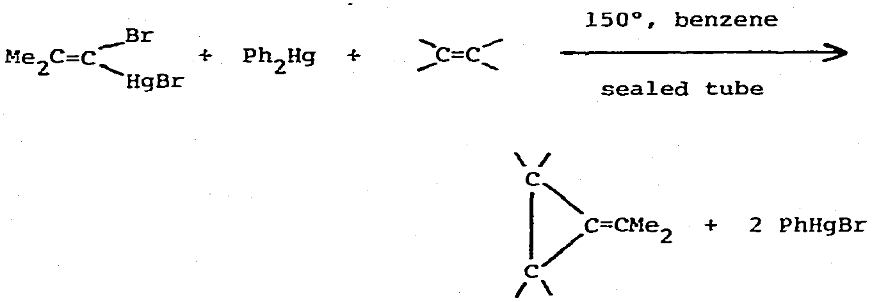


Table 9 summarizes synthetic applications.

More examples of dihalocarbene insertions into Si–H bonds using $PhHgCCl_3$ and $PhHgCBr_3$ have been reported:

$$(Me_3C)_3SiH + PhHgCX_3 \xrightarrow{120°} (Me_3C)_3SiCHX_2 + PhHgX$$

$$(X = Cl,\ Br) \qquad\qquad (55\%)$$

(ref. 61)

$$(Me_2CH)_3SiH + PhHgCCl_3 \xrightarrow[\text{(ref. 62)}]{\text{NaI, } 120°} (Me_2CH)_3SiCHCl_2 + PhHgI + NaCl$$

$$(53\%)$$

$$(cyclo\text{-}C_6H_{11})_3SiH + PhHgCCl_3 \xrightarrow[\text{(ref. 62)}]{120°} (cyclo\text{-}C_6H_{11})_3SiCHCl_2 + PhHgCl$$

$$(53\%)$$

Difluorocarbene transfer to olefins using the $PhHgCF_3/NaI$ reagent continues to be of interest. Moss and Smudin have studied reactions of this mercurial system with trimethylethylene, cyclohexene and olefins 9, 10, 11, 12, 13 and 14 (63). The purpose of this investigation was to determine the relative reactivities of CF_2 toward the C=C bonds in these molecules. Addition of CFCl, derived from $PhHgCCl_2F$, to 14 also was carried out (63). Also

TABLE 9 Divalent Carbon Transfer Reactions of the $Me_2C{=}C(Br)HgBr/Ph_2Hg$ System. From D. Seyferth and D. Dagani, J. Organometal. Chem., 104 (1976) 145.

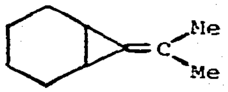
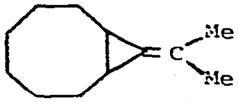
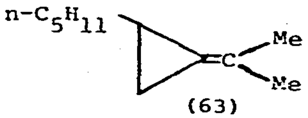
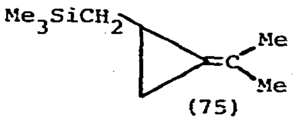
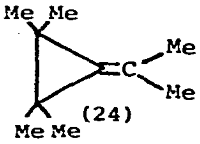
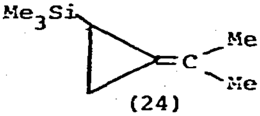
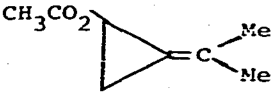
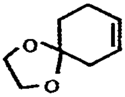
Carbenophile	Reaction time (h)	Product (% yield)	PhHgBr % yield)
Cyclohexene[b]	4	 (87)	95
Cyclooctene[c]	4	 (64)	92
$n\text{-}C_5H_{11}CH{=}CH_2$	18	 (63)	95
$Me_3SiCH_2CH{=}CH_2$	16	 (75)	91
$Me_2C{=}CMe_2$	23	 (24)	95

TABLE 9 (contd.)

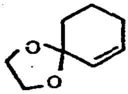
$Me_3SiCH{=}CH_2$[d]	8	 (24)	96
$CH_3CO_2CH{=}CH_2$	16	 (52)	90
Et_3SiH	20	$Et_3SiCH{=}CMe_2$ (97)	94

---

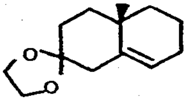
[a] All reactions were carried out at 150°C in a sealed tube with vigorous shaking; 5 mmol each of the mercury reagents and 50 mmol of carbenophile in 10 ml of benzene, unless otherwise noted. [b] 65 mmol. [c] 37 mmol. [d] 9 mmol each of the mercury reagents, 90 mmol of olefin in 15 ml of pentane.



9



10



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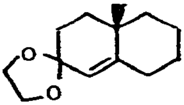
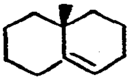
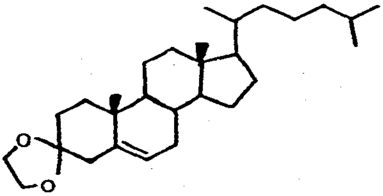


12

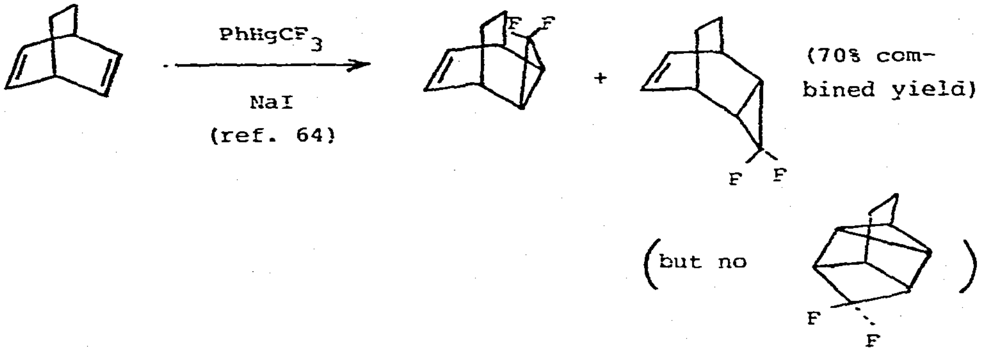


13

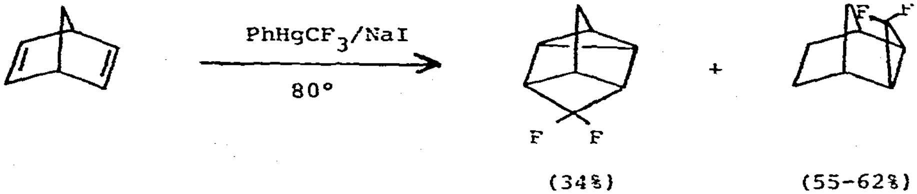


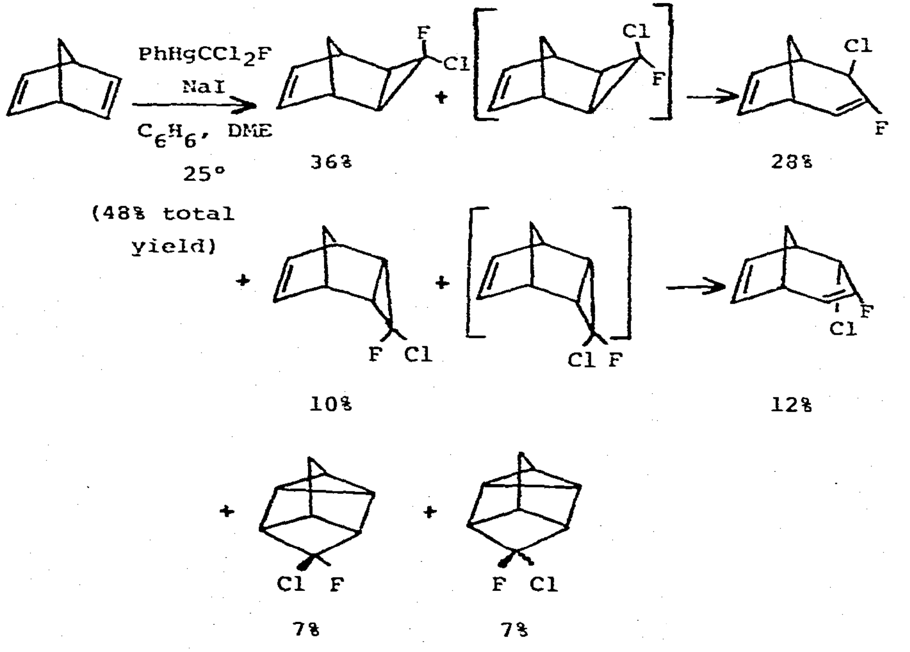
14

reported were reactions of bicyclic dienes with $PhHgCF_3/NaI$: (The use of another current CF_2 source, $[Ph_3PCF_2Br]Br/KF$, gave these adducts in only 20% yield, which demonstrates the efficacy of the $PhHgCF_3/NaI$ system).



In contrast to the above results are the following reactions in which 1,4-addition of CF$_2$ was observed (65):





Bis(trifluoromethyl)mercury has demonstrated utility as a difluorocarbene source. A new preparation of this compound which is interesting but impractical involves fluorination of dimethylmercury (66):

$$(CH_3)_2 \xrightarrow[-78°,\ 5\ days]{F_2/He,\ 1/60\ parts\ by\ vol.} (CF_3)_2Hg \qquad (6.5\%)$$

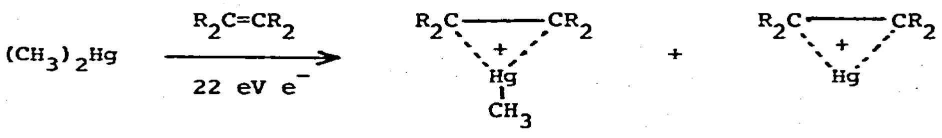
By-products of C-Hg cleavage by fluorine were mercuric fluoride and polyfluoromethanes. Bis(trifluoromethyl)mercury is stable to 3% F_2 in helium at -78°, but it reacted slowly at 0° and rapidly at room temperature with C-Hg cleavage.

4. MERCURATION OF UNSATURATED COMPOUNDS

The mercuration of unsaturated compounds - olefins, acetylenes, cyclopropanes and aromatic compounds - constitutes a major preparative route to organomercurials. Combined with reductive or oxidative demercuration procedures, this general reaction finds useful application in the synthesis of organic compounds, especially of functional derivatives.

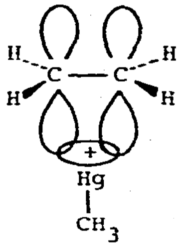
A. Olefins

First we note some studies of a more fundamental nature. The technique of matrix isolation IR spectroscopy was used to confirm the formation of 1:1 complexes between ethylene and mercuric halides at 10°K in argon matrices (67). Insufficient data for a discussion of structure and bonding was available, but the authors opted for "a side-on structure in which the ethylene is bonded to the Hg atom with the C_2H_4 plane parallel and the C=C axis perpendicular to the Hg-X axis". The HgX_2/C_2H_4 interaction becomes weaker in the order $HgF_2 > HgCl_2 > HgBr_2 > HgI_2$, and ethylene is a better σ donor than CO, NO and N_2. It may be that such complexes are intermediates in some olefin mercuration processes. Bach and his coworkers have studied the gas-phase reactivity of olefins toward CH_3Hg^+ cation using ion cyclotron resonance spectroscopy (68). The processes observed were:

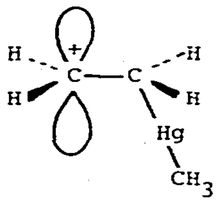


15 16

Ion 16 was only a minor species in the case of ethylene and allene. The relative rate constants for formation of 15 for a number of olefins are given in Table 9a . They show that the rate of mercurinium ion formation increases with increasing methyl substitution on the C=C bond. Extended Hückel MO calculations by these authors indicated that in the gas phase the symmetrical ion 17 was stabilized by 40.9 kcal/mol over the other possibility, 18.



17



18

Of special note is the demonstration by Bloodworth and his coworkers that 1,4-oxymercuration of 1,3-dienes can occur (69):

$$CH_2{=}CH{-}CH{=}CHCH_3 \xrightarrow[MeOH]{Hg(NO_3)_2} \xrightarrow{KCl} ClHgCH_2CH{=}CHCH(OMe)CH_3$$

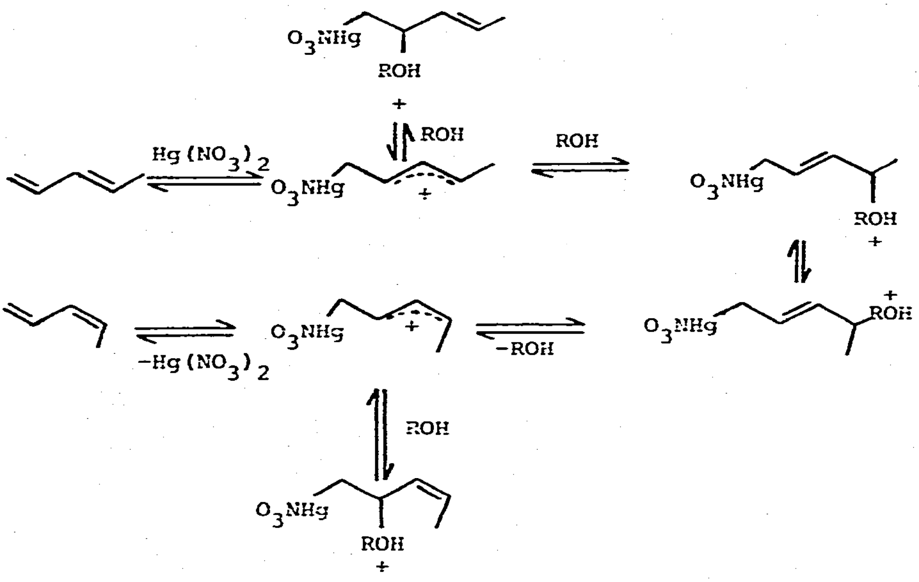
1,4: 2 parts

+

$ClHgCH_2CH(OMe)CH{=}CHCH_3$

1,2: 1 part

Only the 1,2 adduct was formed when mercuric acetate was used in place of mercuric nitrate, but addition of 4 mol % of the nitrate to $Hg(OAc)_2$ sufficed to give the 2:1 ratio of 1,4 to 1,2 addition. The 1,4 isomer thus appears to be formed only under conditions of thermodynamic control. The scheme below was suggested to account for these results:



This scheme provides a pathway for isomerization of the starting diene, and such isomerization was observed experimentally.

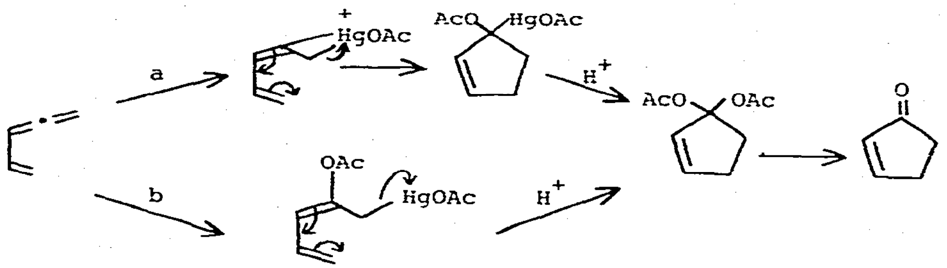
As mentioned in last year's Survey, the olefin oxymer-

TABLE 9a. Rates of Mercurinium Ion Formation. From R.D. Bach, A.T. Weibel, J. Patane and L. Kevan, J. Amer. Chem. Soc., 98 (1976) 6237.

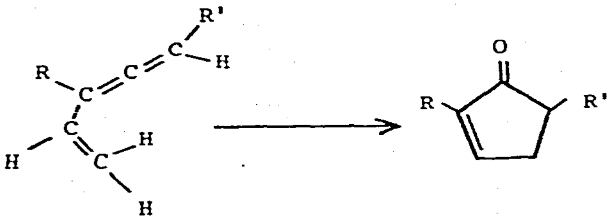
Alkene	k_1 (x $10^{10} cm^3 mol^{-1} s^{-1}$)
$(CH_3)_2C=CH_2$	1.37 ± 0.34
$C_2H_5CH=CH_2$	1.55 ± 0.17
trans-$CH_3CH=CHCH_3$	1.19 ± 0.21
cis-$CH_3CH=CHCH_3$	1.96 ± 0.08
$CH_3CH=C(CH_3)_2$	1.60 ± 0.32
$CH_2=CH-CH=CH_2$	1.37 ± 0.27

curation/demercuration and the oxymercuration/halogenation sequences have become routine organic procedures and exhaustive coverage of this aspect of organomercury chemistry no longer is possible or even necessary. We mention selected examples which have come to our attention during our literature coverage.

Acetoxymercuration of vinylallenes, a route to cyclopentenones, has been reported by French workers (70):



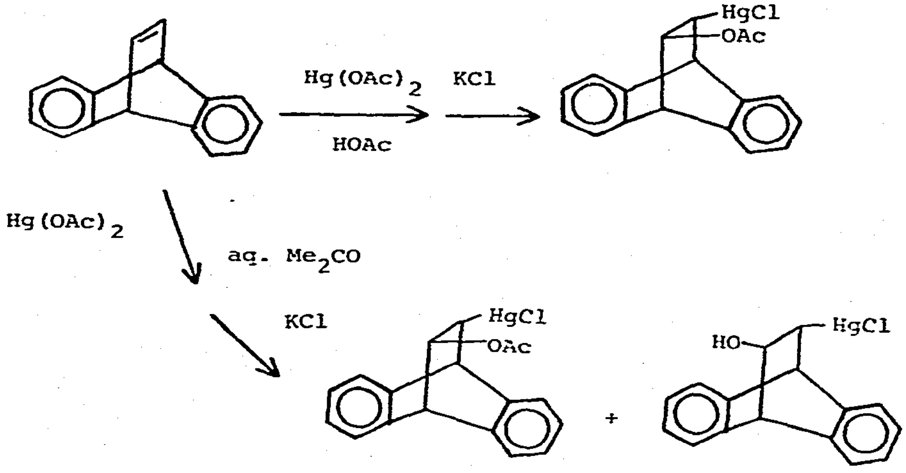
The reaction sequence involves treatment of the vinylallene with mercuric acetate in glacial acetic acid at 25°, followed by addition of perchloric acid. Yields, however, were only moderate at best:

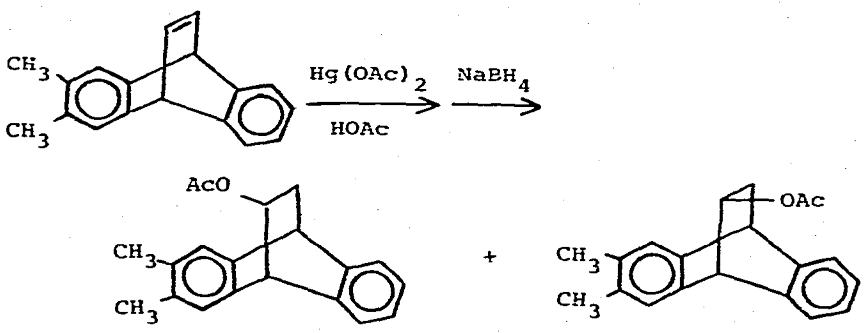


R	R'	% Yield
Me	H	31
Me	Me	20
n-C_5H_{11}	H	59 (70)*
n-C_5H_{11}	Me	42 (50)*

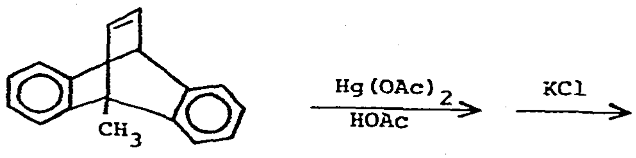
* On heating with $HClO_4$

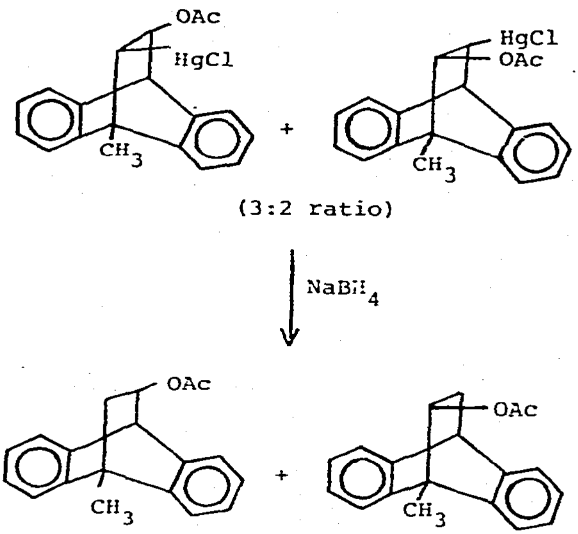
Oxymercuration of some dibenzobicyclo[2.2.2]octatrienes has been studied by two different groups (71, 72):

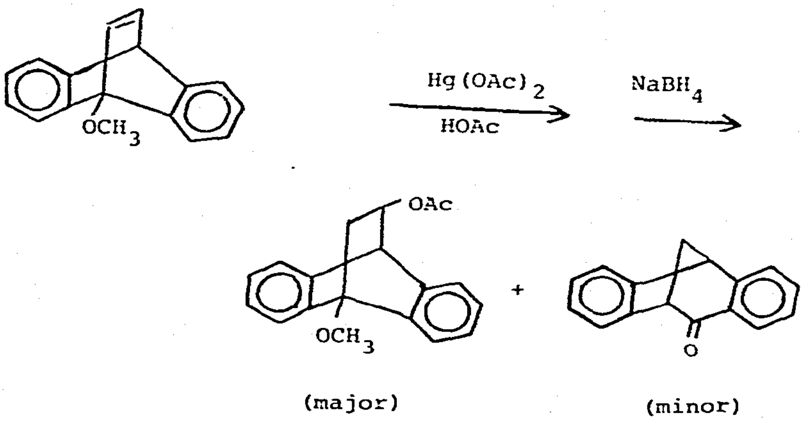




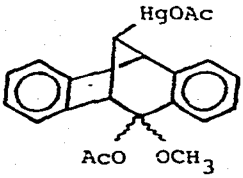
(1:1 ratio)



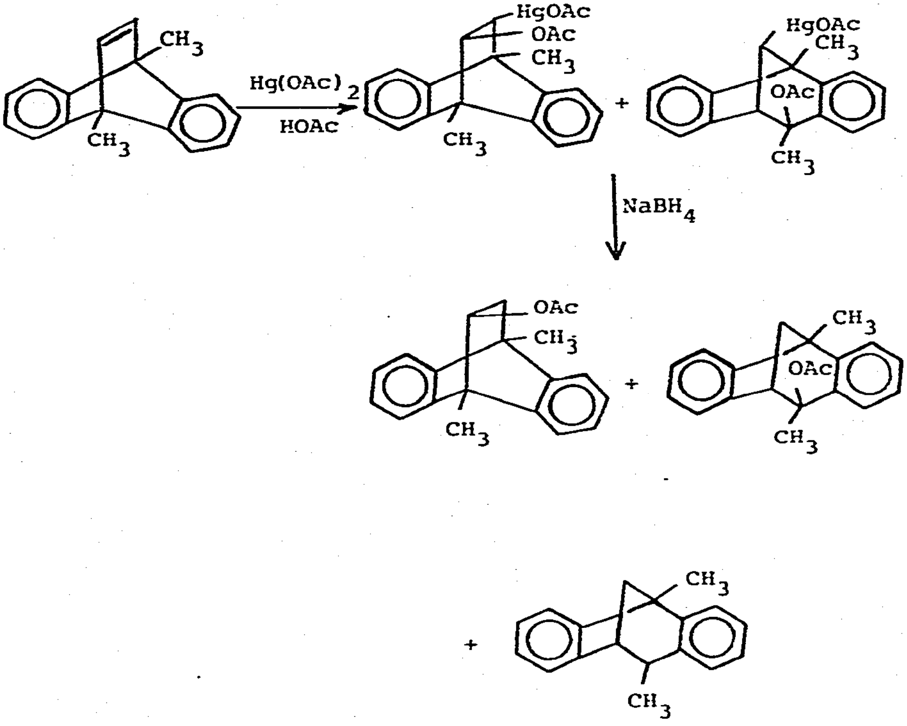


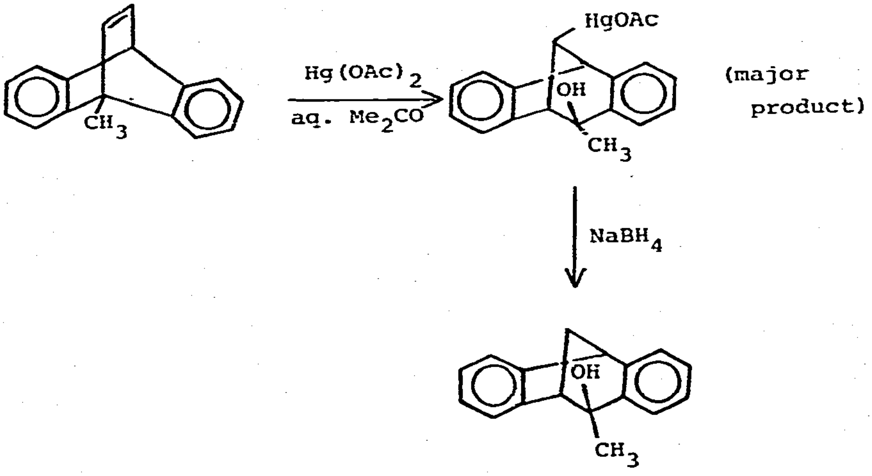


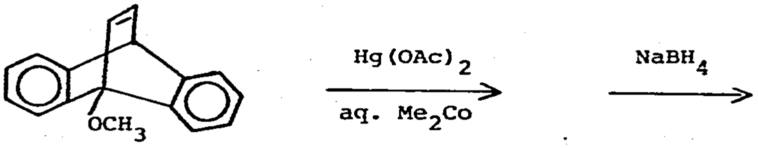
The minor product presumably was formed from mercurial 19 in the work-up and reduction.

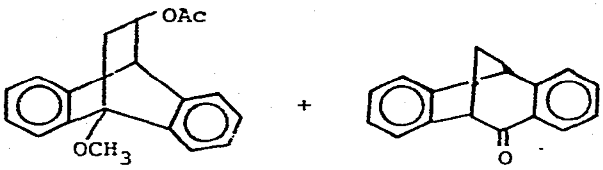


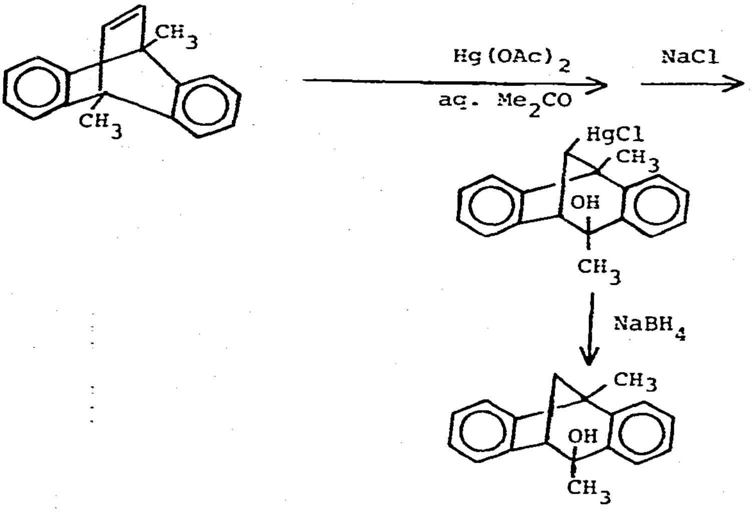
19


CH3
CH3
Hg(OAc)2
HOAc
HgOAc
OAc
CH3
CH3
+
HgOAc
CH3
OAc
CH3
NaBH4
OAc
CH3
CH3
+
CH3
OAc
CH3
+
CH3
CH3


CH3
Hg(OAc)2
aq. Me2CO
HgOAc
OH
CH3
(major
product)
NaBH4
OH
CH3

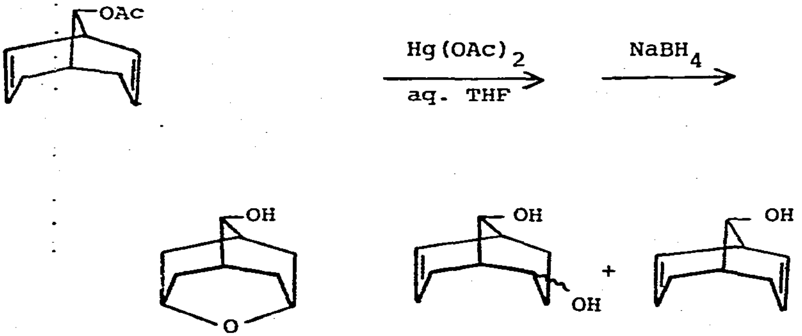

OCH3
Hg(OAc)2
aq. Me2Co
NaBH4





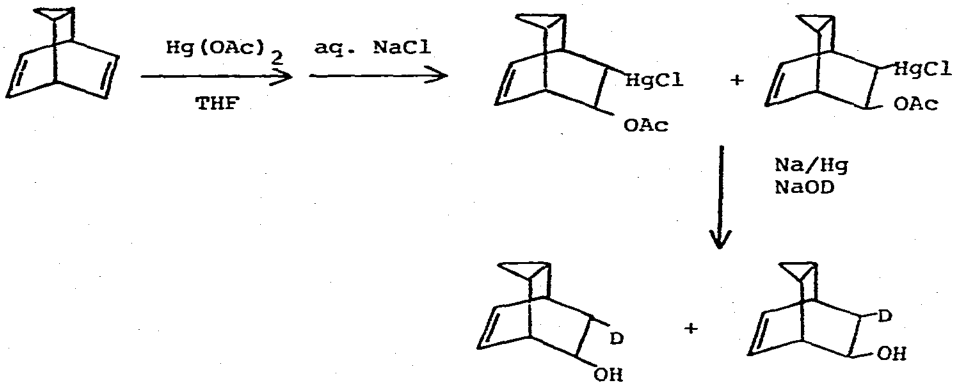
Similar reactions were carried out in other solvent systems. Obviously, multiple mechanisms, including carbocation processes which are accompanied by carbon skeletal rearrangements, are operative.

Oxymercuration-demercuration of 9-acetoxybicyclo[3.3.1]-nona-2,6 (7)-diene has been studied by Moon (73):

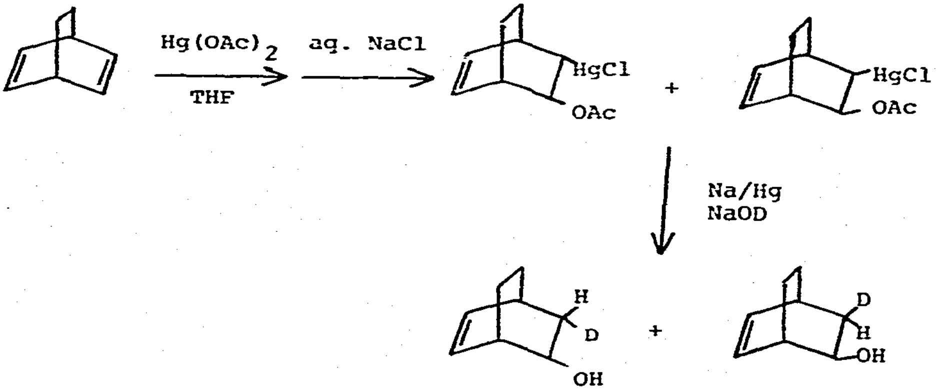


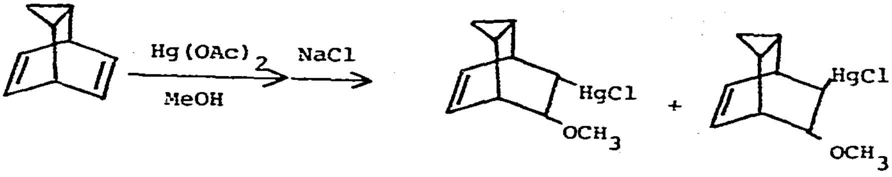
(40%) (45%) (15%)

and the oxymercuration of tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (homobarrelene), bicyclo[2.2.2]octadiene and tricyclo[2.2.2.0^{2,6}] oct-7-ene was investigated by Müller (74):



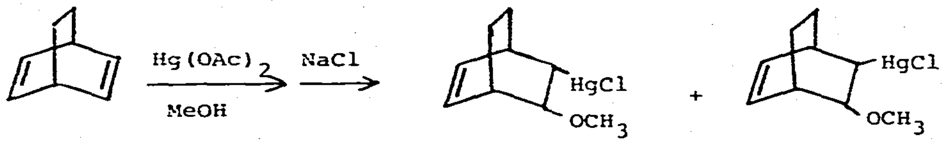
(2,3:1)





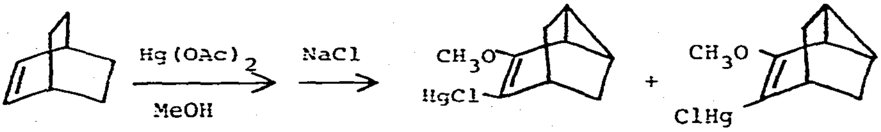
(1.55 : 1)

(+ a mixture of the
corresponding acetates)

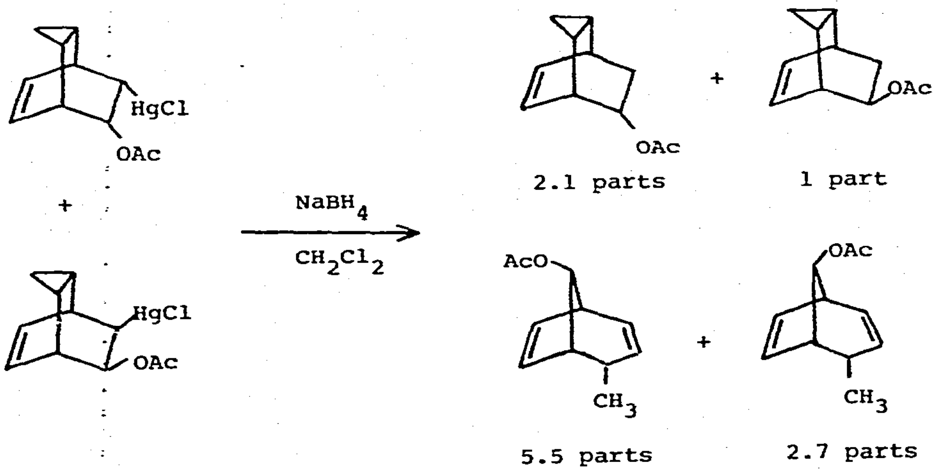


(1.6 : 1)

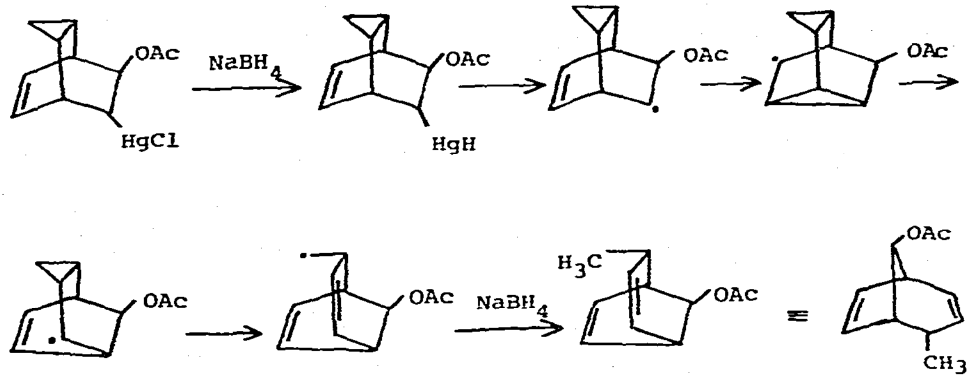
(+ a mixture of the corresponding acetates)



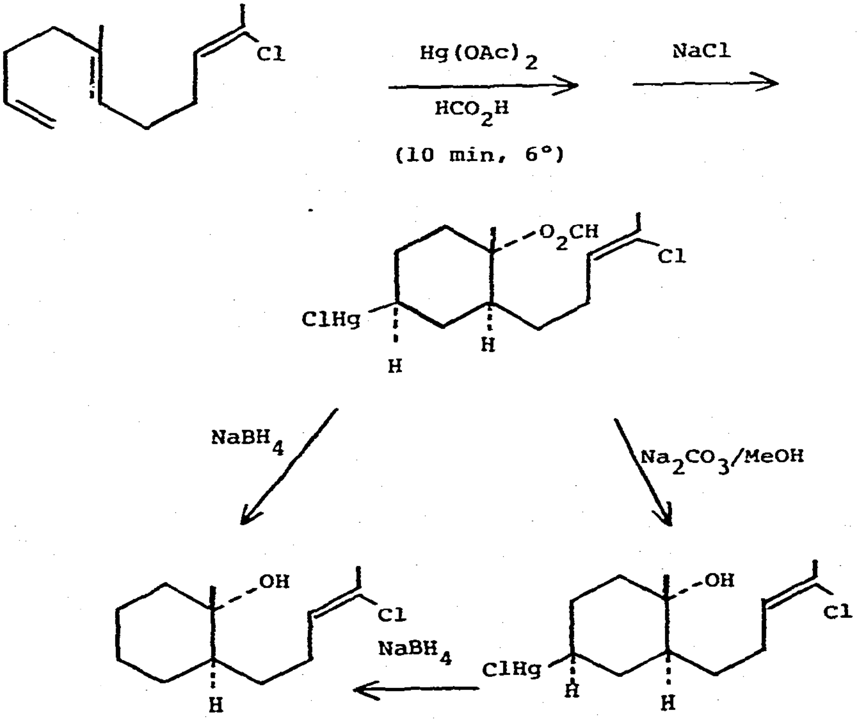
These results were discussed in terms of competitive mercurinium ion (<u>trans</u> addition) and concerted <u>cis</u>-addition mechanisms. The reduction of the oxymercuration product of homobarrelene with metal hydrides ($LiAlH_4$, $NaBH_4$, n-Bu_3SnH) resulted in varying amounts of skeletal rearrangement by way of a radical pathway (75). E.g., with $NaBH_4$:



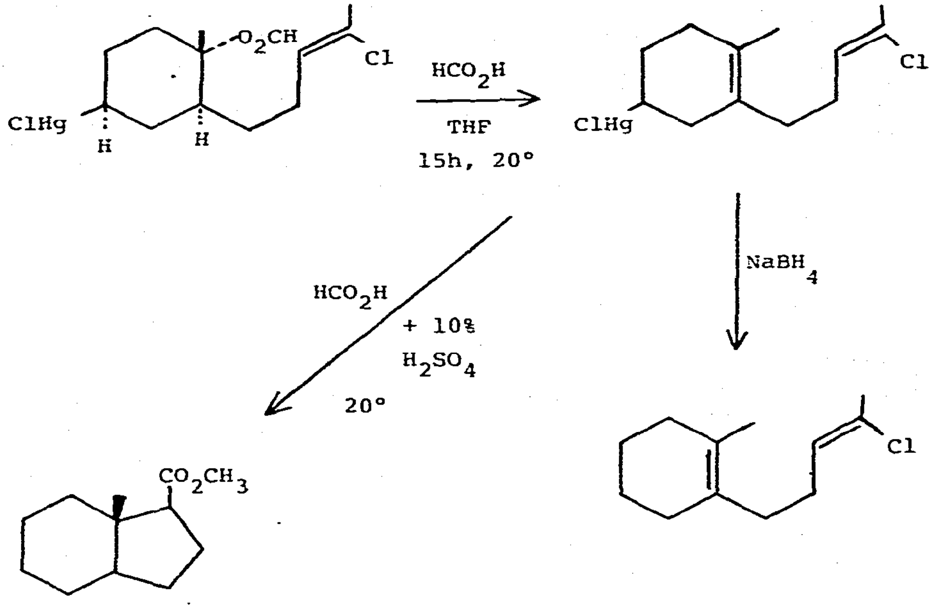
via:



Stereoselective cyclizations were accomplished by means of oxymercuration processes (76):

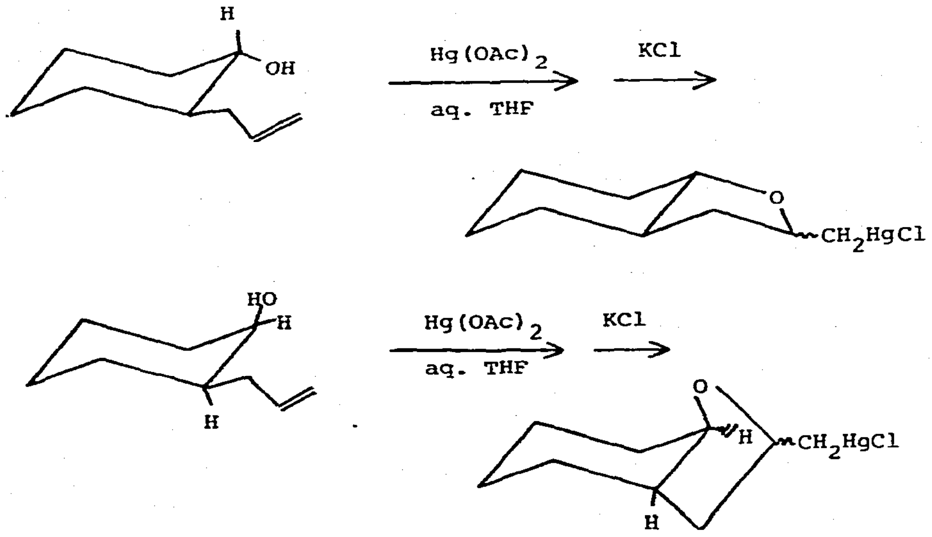


and:

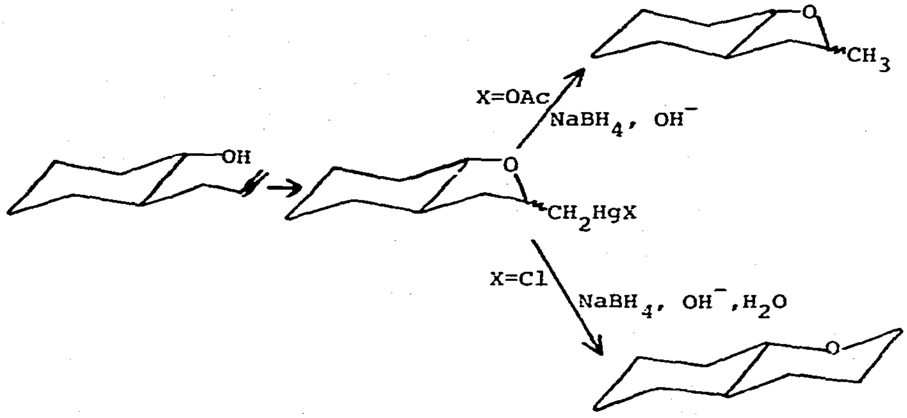


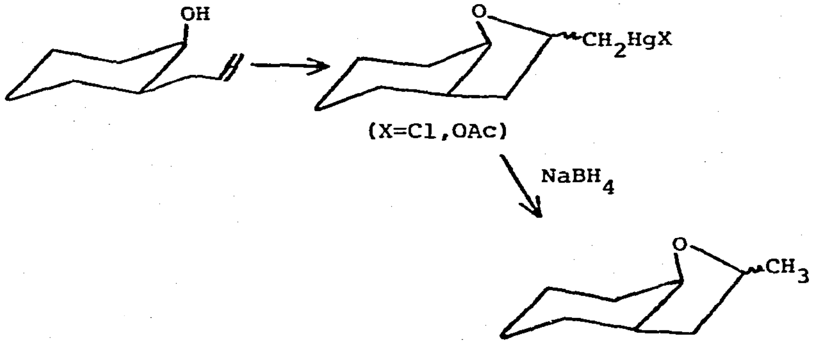
(mixture of *cis* and *trans* isomers)

French workers have reported the preparation of bicyclic systems by intramolecular oxymercuration of *cis*- and *trans*-2-allylcyclohexanols (77):

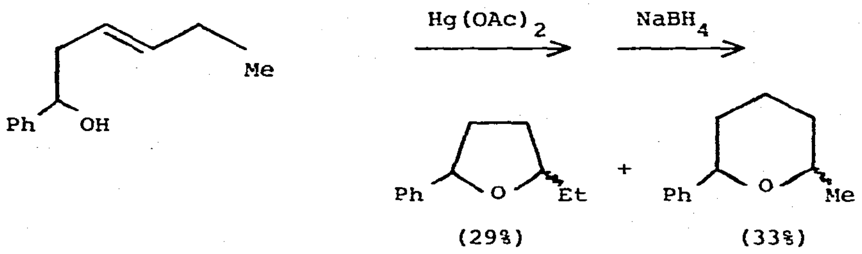


Five-membered rings were formed with both isomers, but the reactions are not stereoselective. Sodium borohydride reduction gave either tetrahydrofuran or tetrahydropyran derivatives, depending on the conditions used:





Formation of both 5- and 6-membered cyclic ethers in alkenol oxymercuration-demercuration also was observed by Japanese workers (78):



Solvomercuration of 3-methyl-5α-cholest-2-ene and other steroidal olefins was studied by Holtmeier and Welzel (79). Equilibrium constants for the (reversible) addition of mercuric trifluoroacetate in benzene-d_6 and in THF were determined by NMR techniques (Table 10). Although the equilibrium constant for this reaction of 3-methyl-5α-cholest-2-ene is small and the oxymercuration of this compound could not be effected under "normal" conditions in aqueous THF, adjustment of the pH of the reaction medium to 3.5 by addition of NaOH allowed the isolation of the oxymercuration-$(NaBH_4)$dehydromercuration product of this olefin in moderate yield. pH Adjustment in olefin oxymercuration is an old trick that dates back to 1900, and so this result is hardly surprising. Similar observations were made in the case of 5α-cholest-2-ene, in that pH adjustment was necessary in order to effect good product yields (80).

The mercuration of "benzene tautomers", which proceeds with aromatization of the six-membered ring to give benzylmercury derivatives, has received further study by Reutov and his coworkers (81-83):

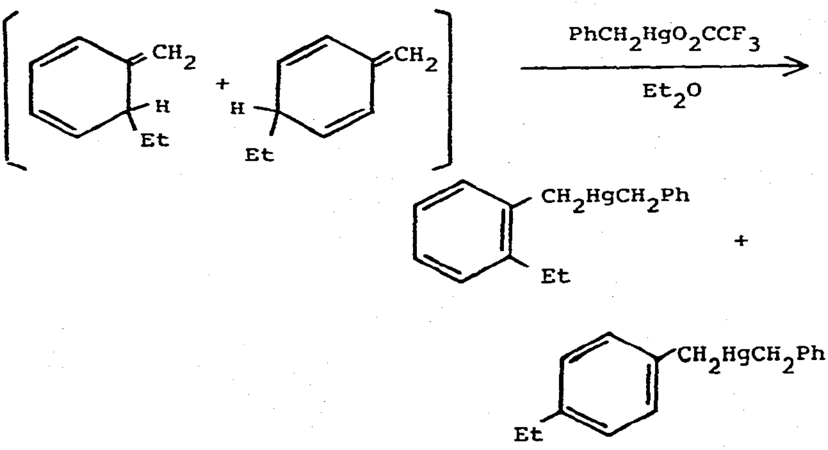
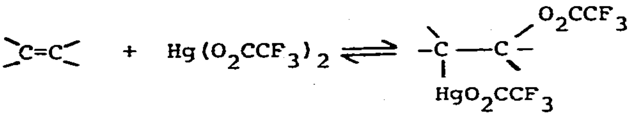
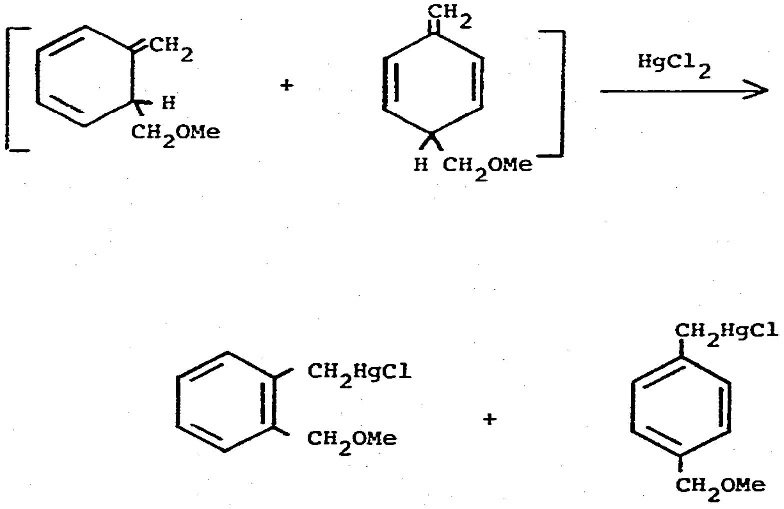


TABLE 10. Equilibrium Constants of Reactions of Some Olefins with Mercuric Trifluoroacetate in Aprotic Media. From W. Holtmeier and P. Welzel, Tetrahedron Lett. (1976) 3423.

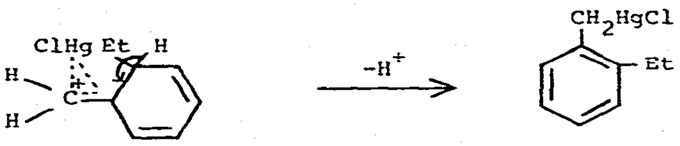


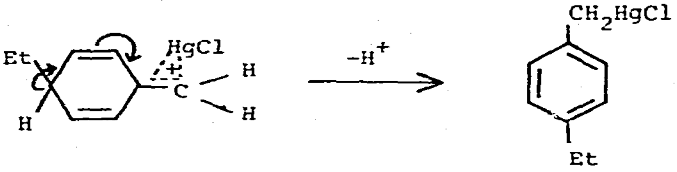
Olefin	K (Benzene)	K (THF)
5α-Cholest-2-ene	430[a]	0.6[c]
3-Methyl-5α-cholest-2-ene	1.6[a]	
4-Cholestene	36 [a]	
5-Cholestene	3.8[b]	
3β-Acetoxy-5α-pregn-14-en-20-one	2.2[a]	
Cyclohexene	1330	38
1-Methylcyclohexene		4.4
Cyclopentene		3.4

a) at 10°C; b) at 12°C; c) at 8°C

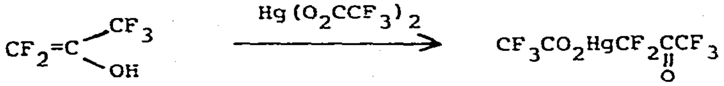


It is assumed that the proton is eliminated in such processes as shown below:

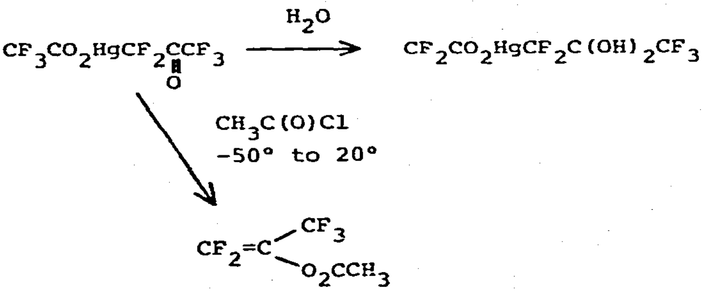


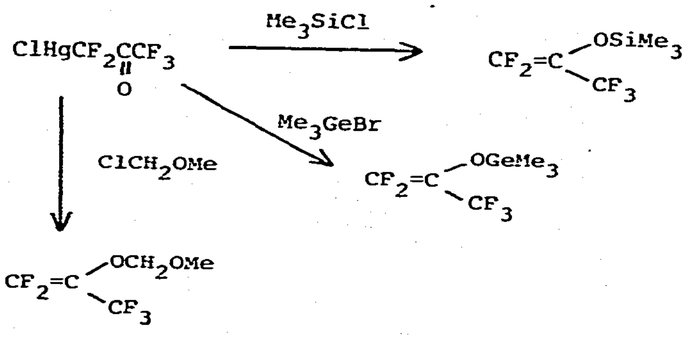


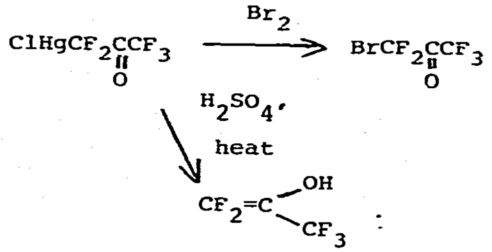
Some other mercurations of interest include the following. Perfluoro-2-propenol (84):



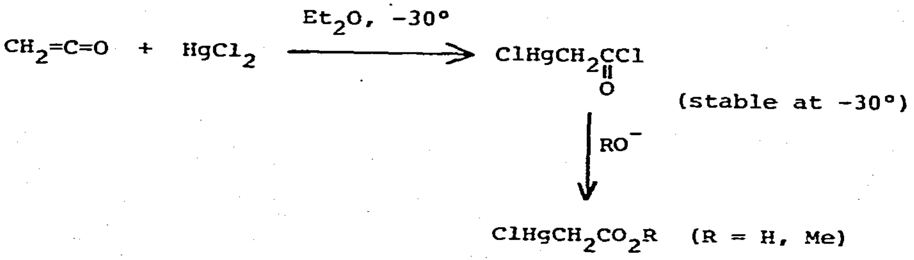
Further reactions of the product and its derivatives were studied:



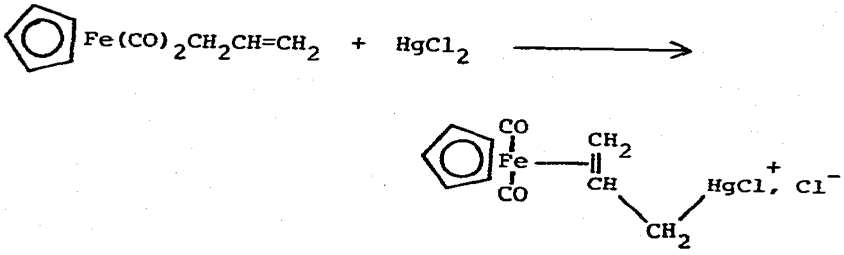




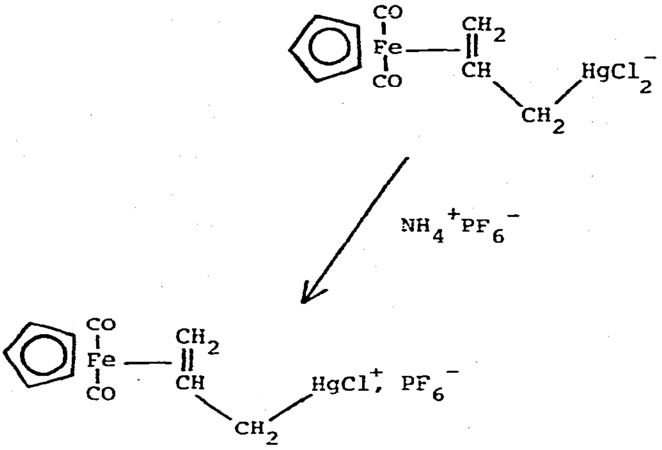
Ketene (85):



An allyl-iron compound (86):



or



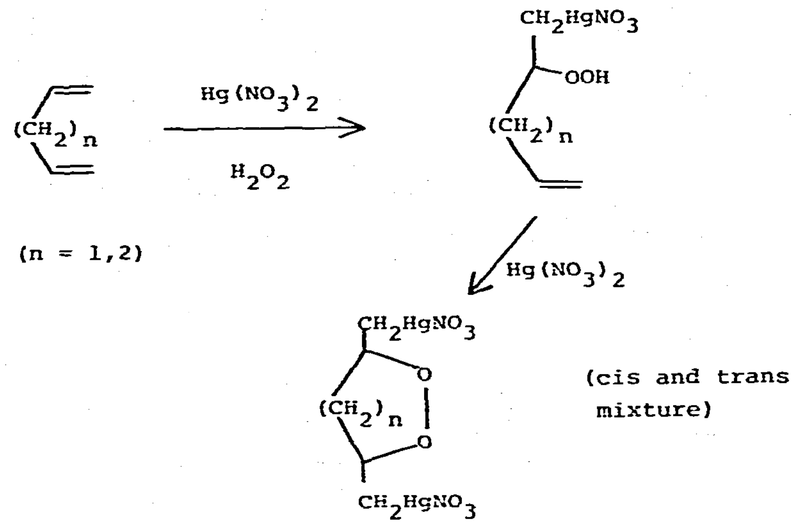
π-$C_5H_5Fe(CO)_2CH_2CMe{=}CH_2$ reacted similarly, but with π-C_5H_5-$Fe(CO)_2CH_2CH{=}C(CH_3)_2$ and π-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, the major or sole product was π-$C_5H_5Fe(CO)_2HgCl$ as a result of electrophilic attack by $HgCl_2$ at the Fe atom rather than at the C=C bond. In this case, the σ-allyl group was displaced as a carbonium ion.

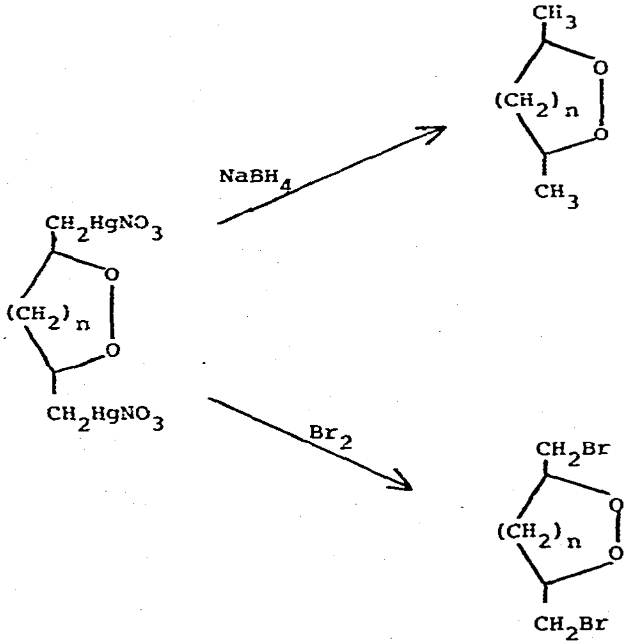
Allylurea, with $^{197}Hg(OAc)_2$ to give labelled Neohydrin (87):

$$CH_2{=}CHCH_2NHC(O)NH_2 + {}^{197}Hg(OAc)_2 + H_2O \longrightarrow \xrightarrow{NaCl} Cl^{197}HgCH_2CH(OH)CH_2NHC(O)NH_2$$

(Neohydrin is used as a topographic agent in kidney scintigraphy since it accumulates in kidney parenchyme with high selectivity).

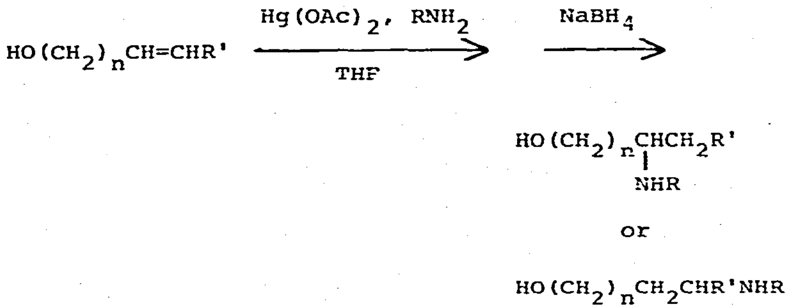
While hydroxy- and alkoxymercuration are the most extensively practised solvomercuration processes, the introduction of nucleophilic fragments other than OH^- and OR^- in conjuction with the electrophilic mercury moiety, HgX^+, can be useful in synthesis. Among such processes, peroxymercuration has been developed in recent years by Reutov et al. and Bloodworth et al. From the latter group comes a study of the peroxymercuration of nonconjugated dienes which provides a simple route to cyclic peroxides (88):





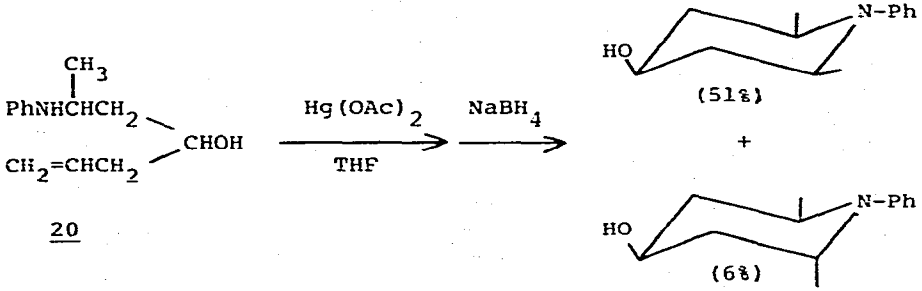
Mercuric trifluoroacetate is less effective in this application than is mercuric nitrate.

New examples of the aminomercuration reaction have been reported by French workers. Among these is a route to aminoalcohols via aminomercuration-demercuration (89):



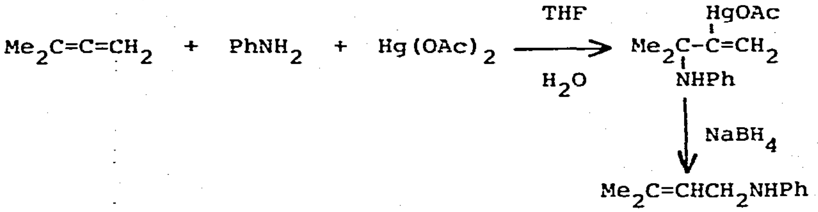
$$HO(CH_2)_nCH{=}CHR' \xrightarrow[THF]{Hg(OAc)_2,\ RNH_2} \xrightarrow{NaBH_4} HO(CH_2)_nCH(NHR)CH_2R' \text{ or } HO(CH_2)_nCH_2CHR'NHR$$

Table 11 brings examples of such reactions in which aniline was the amine used. The cyclization of 20 using aminomercuration could be accomplished:



20

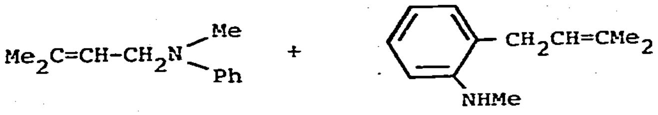
The same group has investigated the aminomercuration of allenes (90):



$$Me_2C{=}C{=}CH_2 + PhNH_2 + Hg(OAc)_2 \xrightarrow[H_2O]{THF} Me_2C(NHPh){-}C(HgOAc){=}CH_2 \xrightarrow{NaBH_4} Me_2C{=}CHCH_2NHPh$$

(The demercuration proceeds with rearrangement).

$$Me_2C{=}C{=}CH_2 + PhNHMe + Hg(OAc)_2 \xrightarrow[H_2O]{THF} \xrightarrow{NaBH_4}$$



(1:1 ratio)

TABLE 11. Aminomercuration of Unsaturated Alcohols. From H. Hodjat-Kachani, J. J. Perie and A. Lattes, Chem. Lett. (1976) 409.

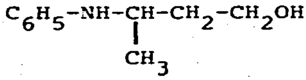
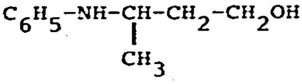
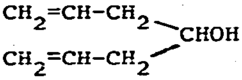
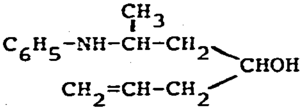
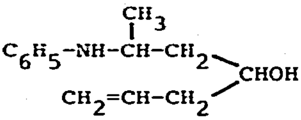
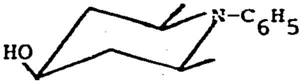
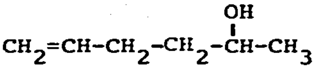
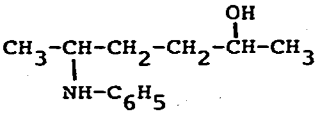
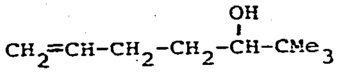
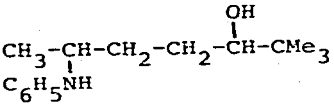
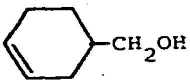
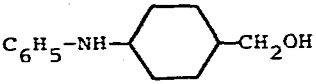
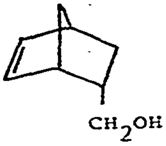
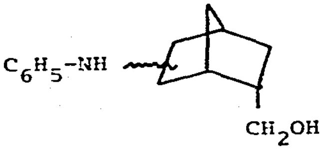
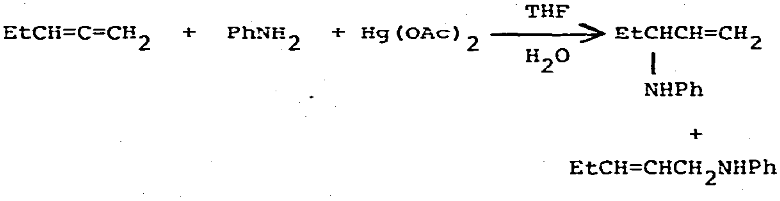
Starting Ethylenic Alcohols	Amino-alcohols	Yields %
$CH_3-CH=CH-CH_2OH$	 $C_6H_5-NH-\underset{CH_3}{CH}-CH_2-CH_2OH$	52
$CH_2=CH-CH_2-CH_2OH$	 $C_6H_5-NH-\underset{CH_3}{CH}-CH_2-CH_2OH$	68
		63
		7
		51
		6
 $CH_2=CH-CH_2-CH_2-\overset{OH}{CH}-CH_3$	 $CH_3-\underset{NH-C_6H_5}{CH}-CH_2-CH_2-\overset{OH}{CH}-CH_3$	35

TABLE 11 (contd.)

 $CH_2=CH-CH_2-CH_2-CH(OH)-CMe_3$	 $CH_3-CH(NHC_6H_5)-CH_2-CH_2-CH(OH)-CMe_3$	30
		57
		30

The *ortho*-allylated product was believed to result from a Claisen-like rearrangement of the tertiary allylic amine product.

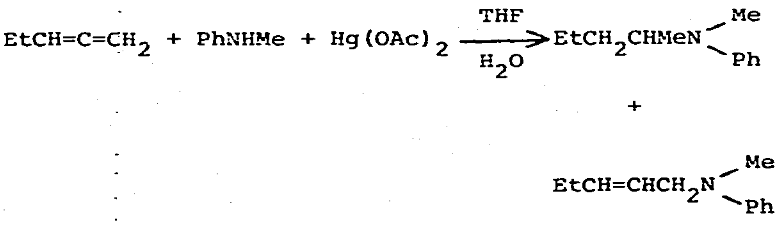


$$EtCH=C=CH_2 + PhNH_2 + Hg(OAc)_2 \xrightarrow[H_2O]{THF} EtCH(NHPh)CH=CH_2 + EtCH=CHCH_2NHPh$$

(1:4 ratio)

$$CH_2=C=CH_2 + PhNH_2 + Hg(OAc)_2 \xrightarrow[H_2O]{THF} PhNHCH_2CH=CH_2$$

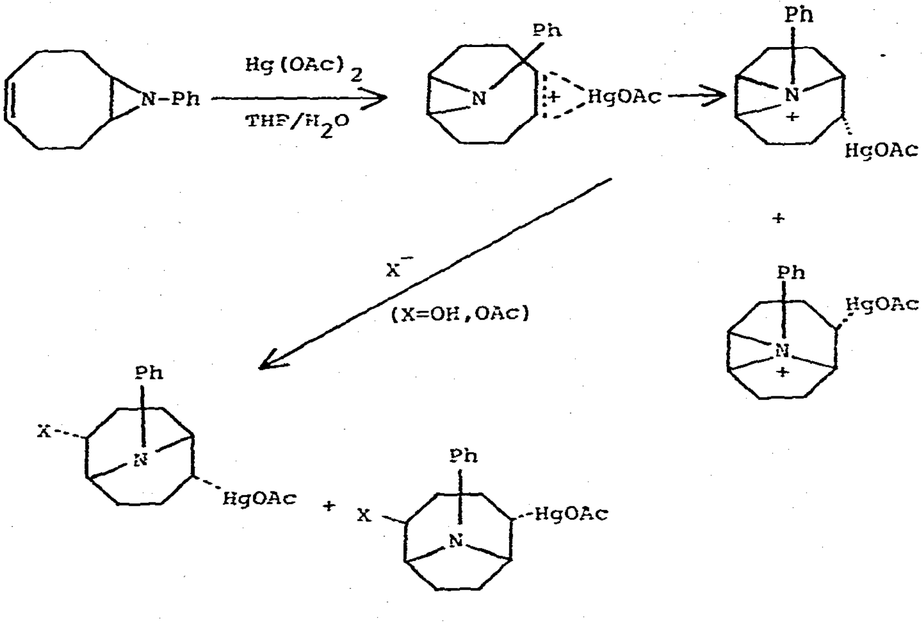
(10%)



$$EtCH=C=CH_2 + PhNHMe + Hg(OAc)_2 \xrightarrow[H_2O]{THF} EtCH_2CHMeN(Me)Ph + EtCH=CHCH_2N(Me)Ph$$

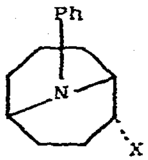
(*cis* and *trans*)

Other workers studied the aminomercuration of 9-N-phenylazabicyclo[6.1.0]non-4-ene (91):



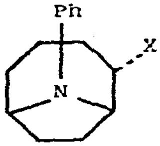
(trace)

Sodium borohydride reduction of the product gave 21 and traces of 22.



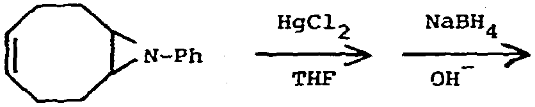
(X=OH, OAc)

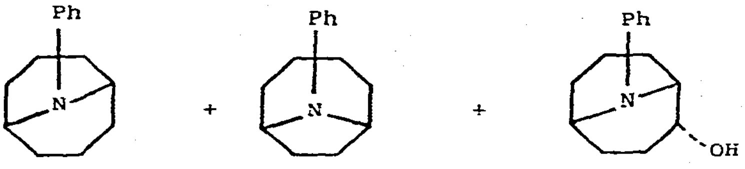
21



(X=OH, OAc)

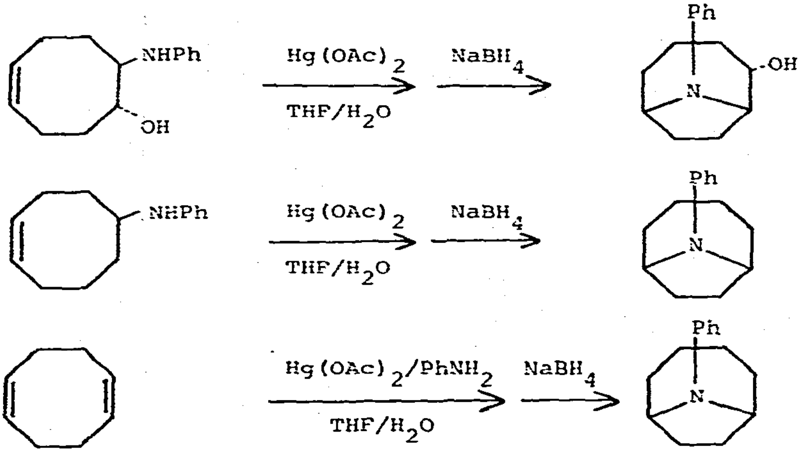
22





(40%) (10%) (50%)

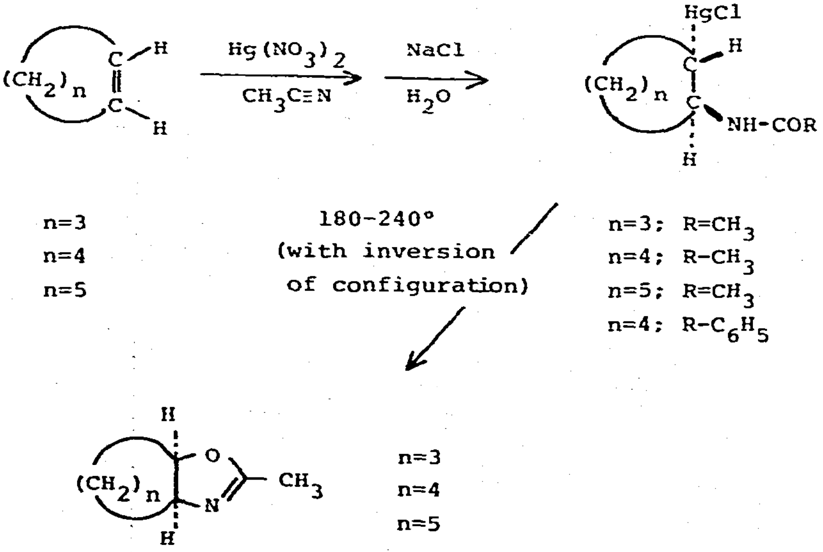
also:

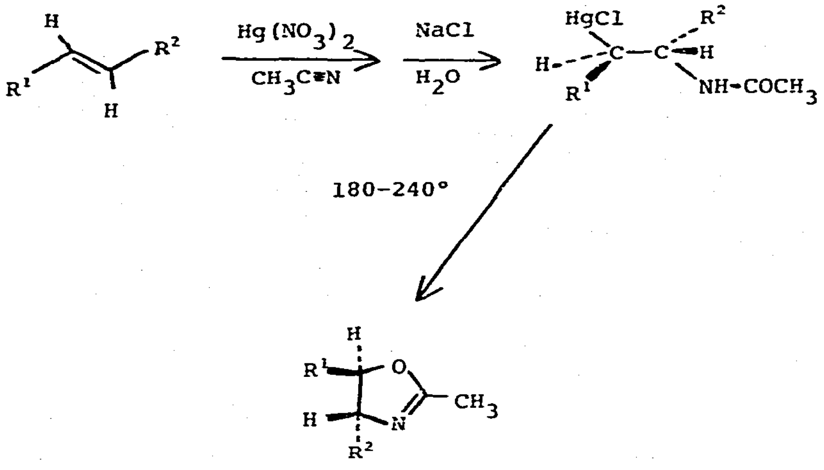


(60%)

(10%)

The amidomercuration reaction has been used by Kretchmer and Daly in the synthesis of 2-oxazolines (92):

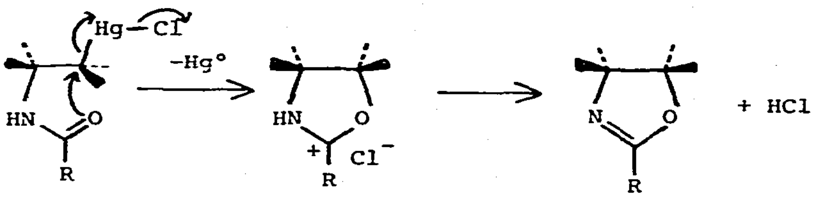




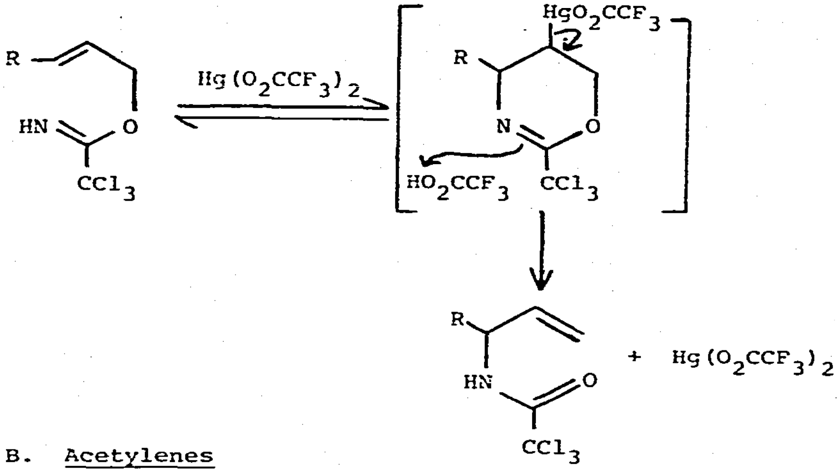
$R^1=R^2=C_3H_7$

$R^1=H;\ R^2=C_6H_{13}$

The yields of the oxazolines, however, were only moderate (10-30%) and in some cases thermal deacylaminomercuration gave back substantial amounts of the starting olefin. The thermolysis of the amidomercuration products was pictured as proceeding as shown below:



Finally, we note the mercury(II)-salt- catalyzed rearrangements of allylic trichloroacetimidates (93) and allylic N,N-dimethylcarbamates (94), which must involve olefin mercuration intermediates in an iminomercuration-deoxymercuration sequence in the former case, e.g.:

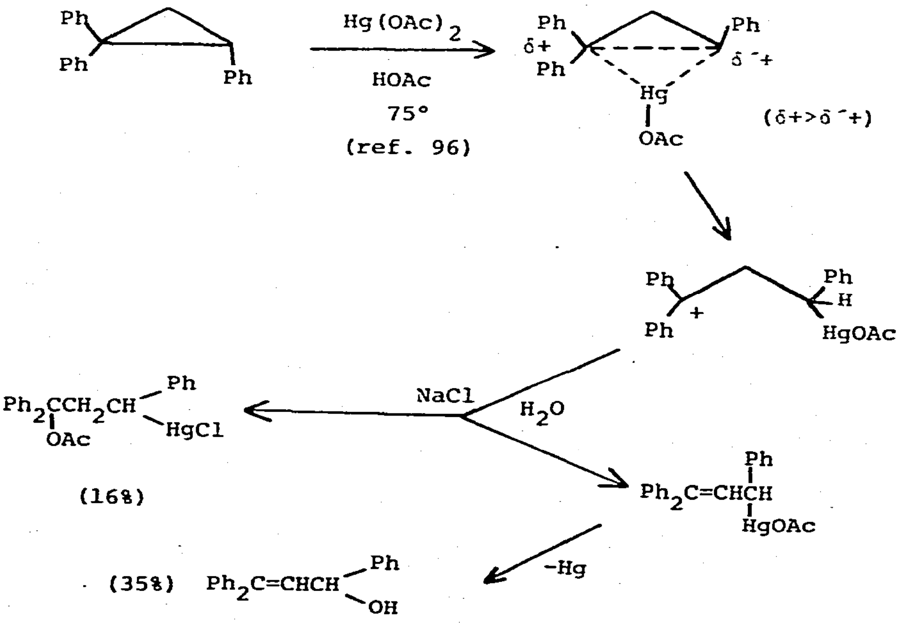


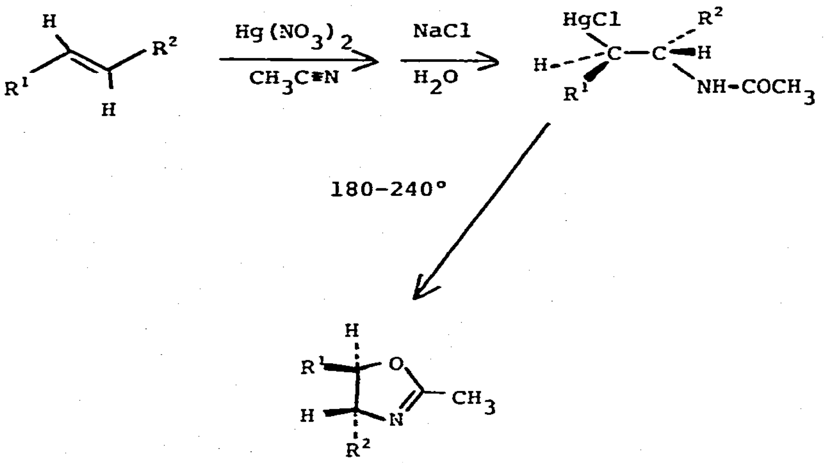
B. Acetylenes

French workers have studied the hydration of vinylacetylene catalyzed by inorganic and arylmercuric salts (95). Organomercury intermediates are known to be involved in such processes.

C. Cyclopropanes

Russian workers of the Moscow State University have continued their studies of the action of mercuric acetate on phenylcyclopropanes:





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$R^1=H;\ R^2=C_6H_{13}$

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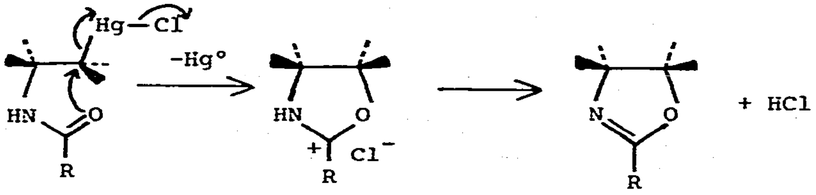

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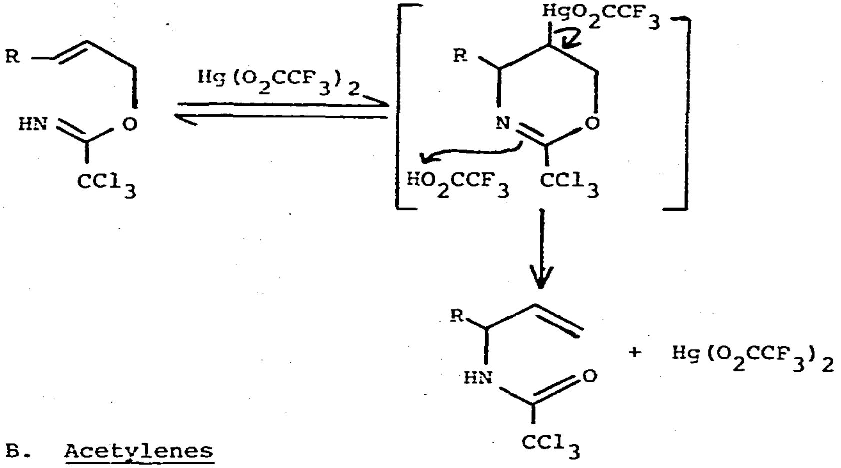

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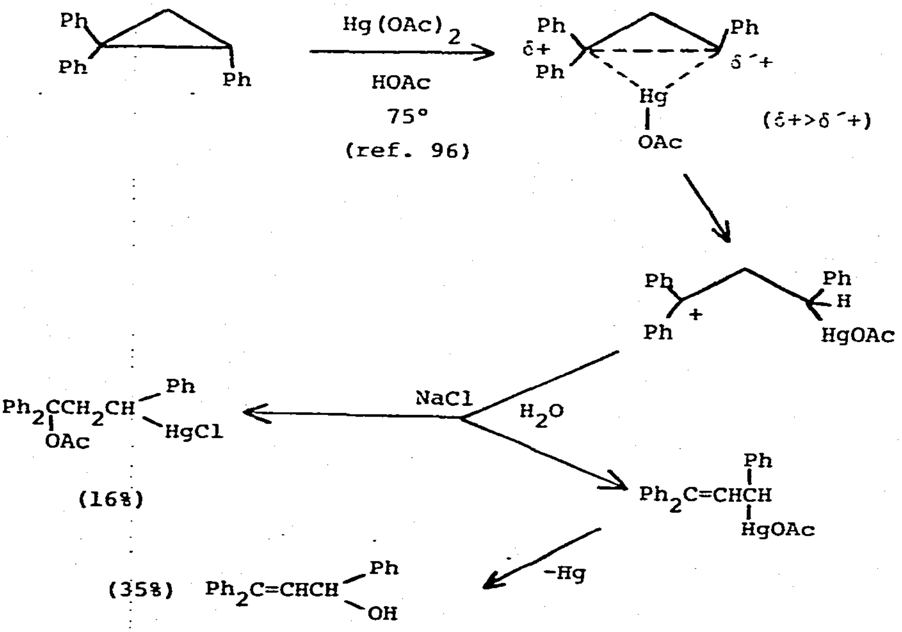
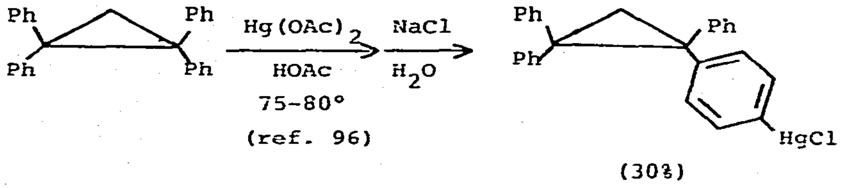
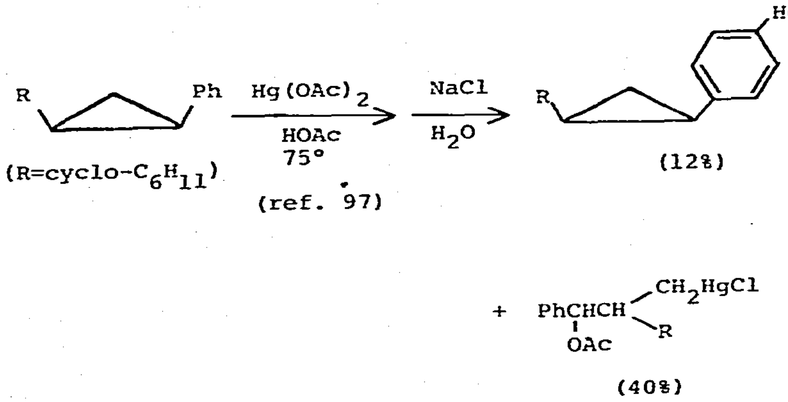
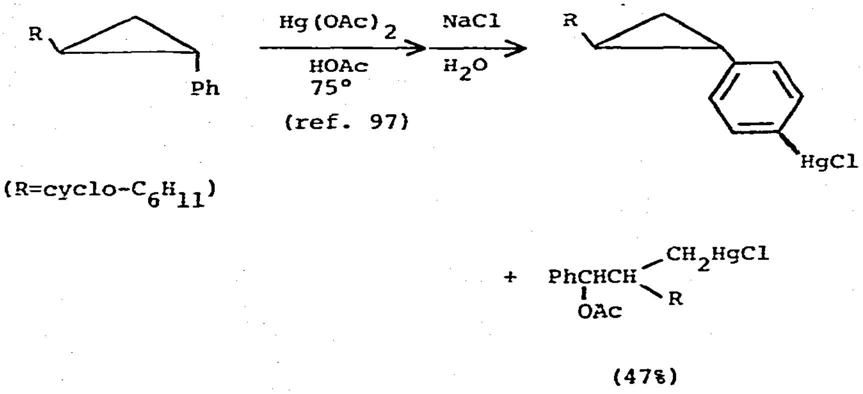


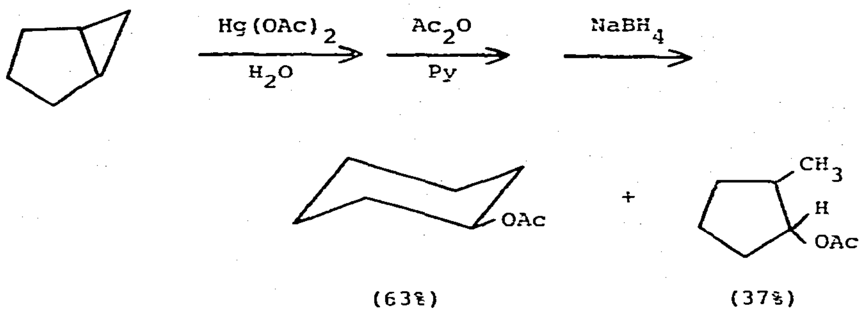
but:

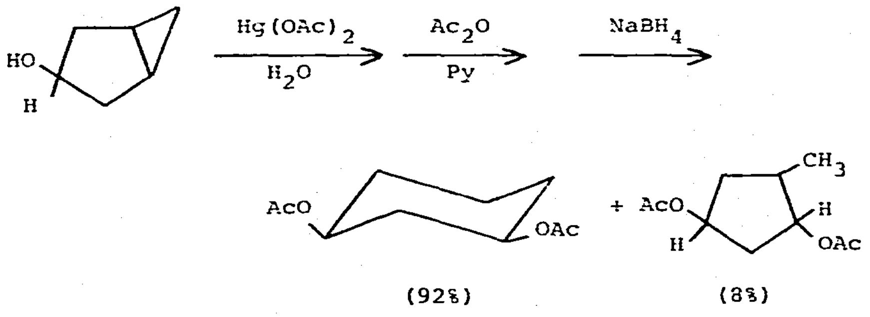


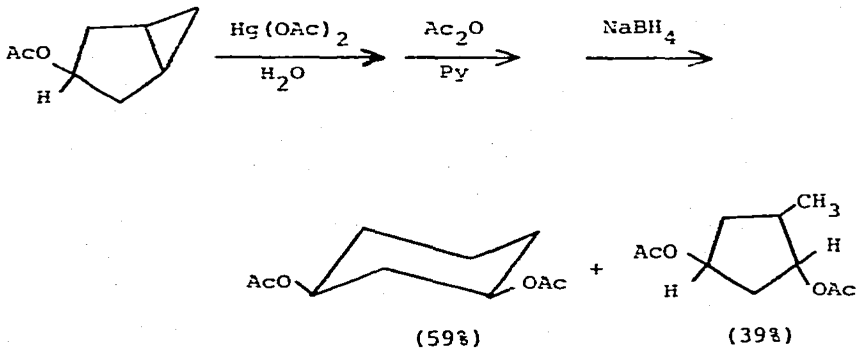


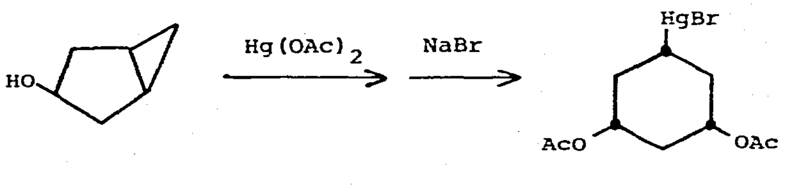


In the oxymercuration of bicyclo[3.1.0]hexanes, zero-bridge cleavage was found to be the major process occurring (98), in contrast to previous reports by others.


Hg(OAc)$_2$
H$_2$O
Ac$_2$O
Py
NaBH$_4$
OAc
+
CH$_3$
H
OAc
(63%)
(37%)

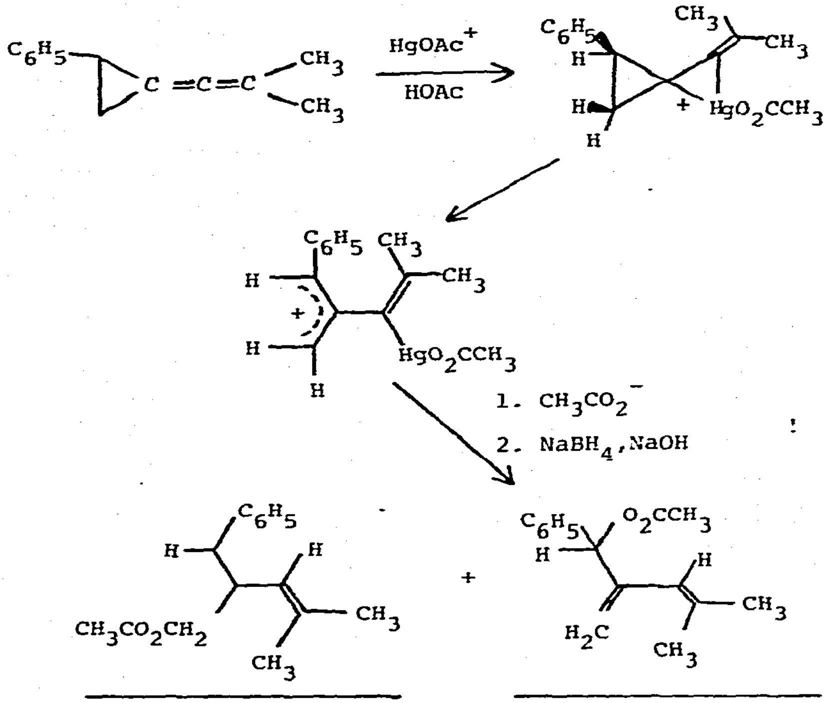

HO
H
Hg(OAc)$_2$
H$_2$O
Ac$_2$O
Py
NaBH$_4$
AcO
OAc
+ AcO
H
CH$_3$
H
OAc
(92%)
(8%)


AcO
H
Hg(OAc)$_2$
H$_2$O
Ac$_2$O
Py
NaBH$_4$
AcO
OAc
+
AcO
H
CH$_3$
H
OAc
(59%)
(39%)

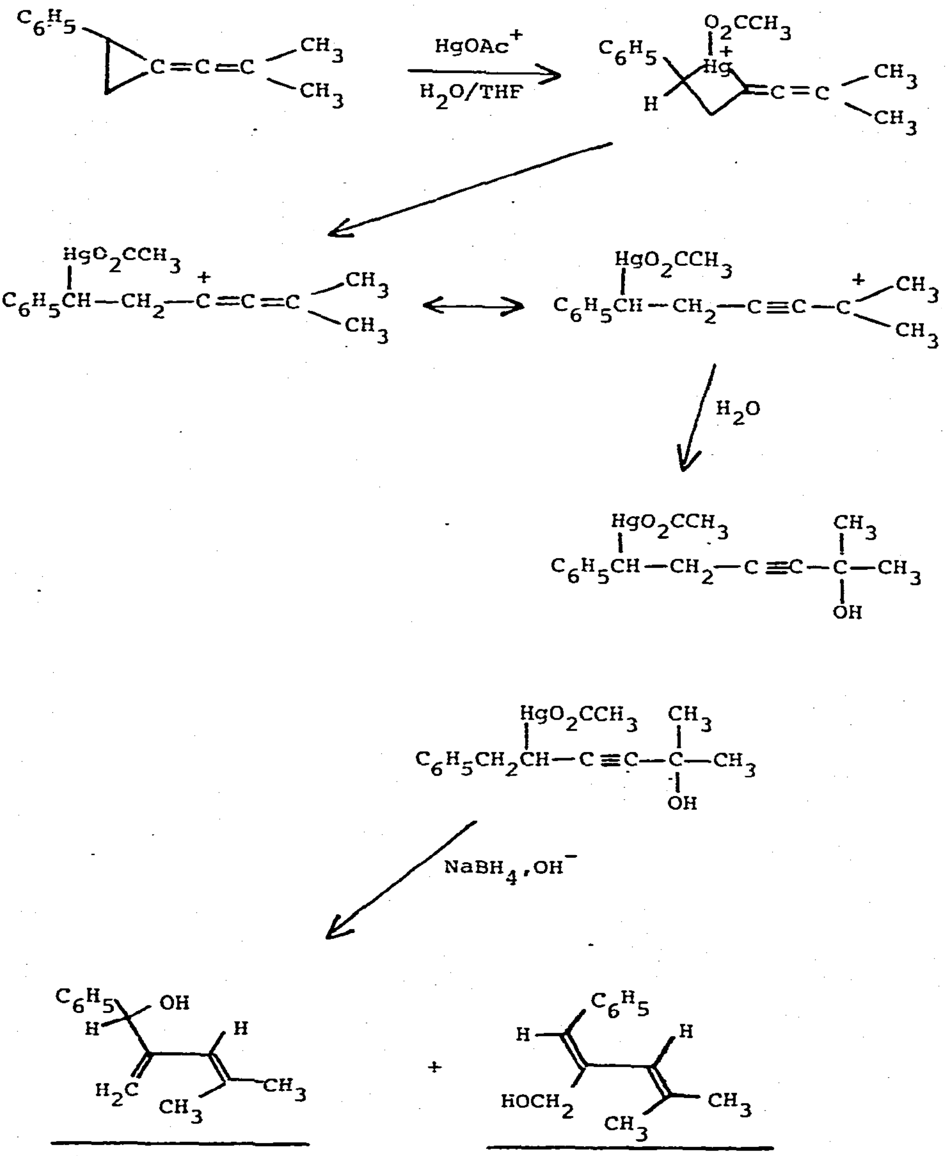

HO
Hg(OAc)$_2$
NaBr
HgBr
AcO
OAc

Halogenolysis in pyridine and proton NMR served in product structure determination.

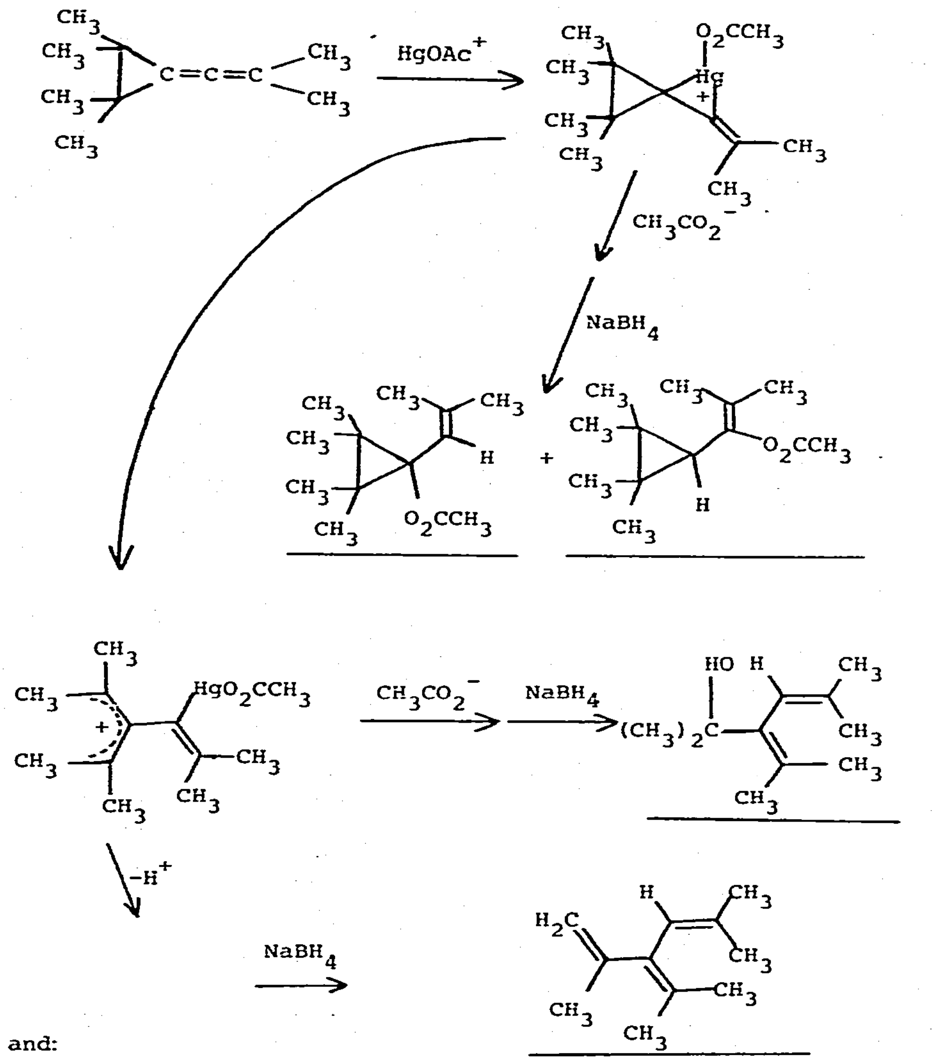
Acetoxy- and hydroxymercuration of an alkenylidenecyclopropane proceeded with ring opening (99):



+ dimeric acetates

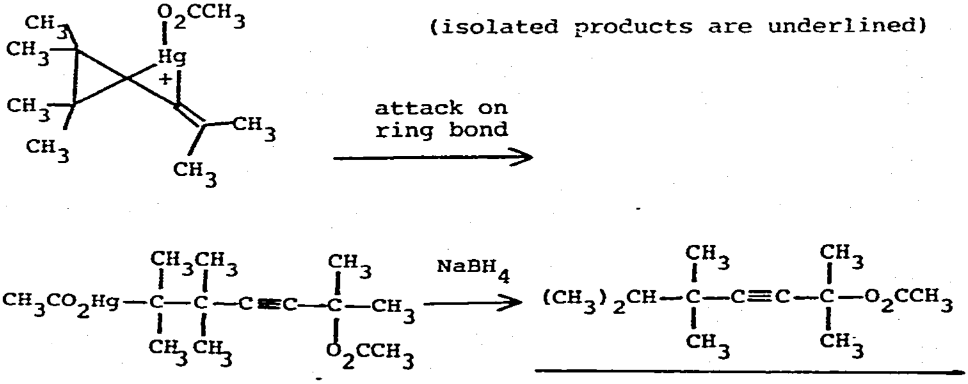


HgOAc⁺
H₂O/THF
H₂O
NaBH₄,OH⁻

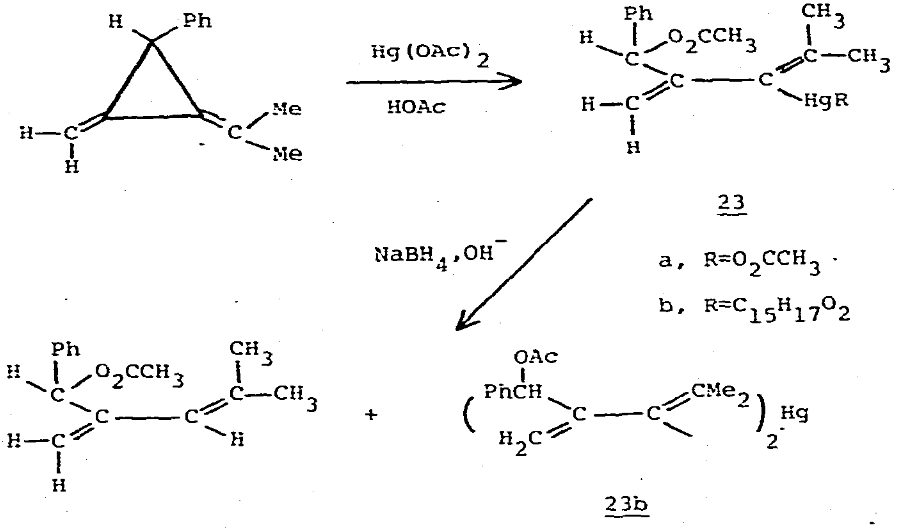


(isolated products are underlined)

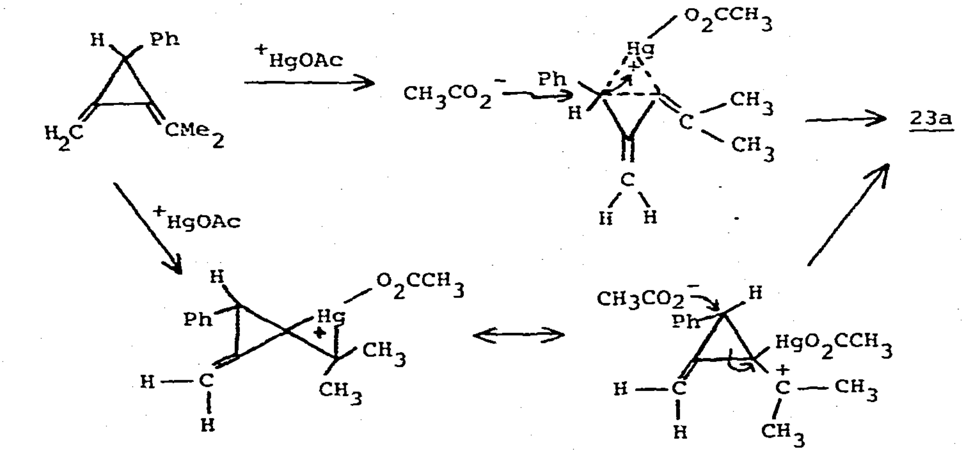
and:



The acetoxymercuration-demercuration of a bisalkylidenecyclopropane gave not only a reduced acetoxy product but also an organomercurial (100):

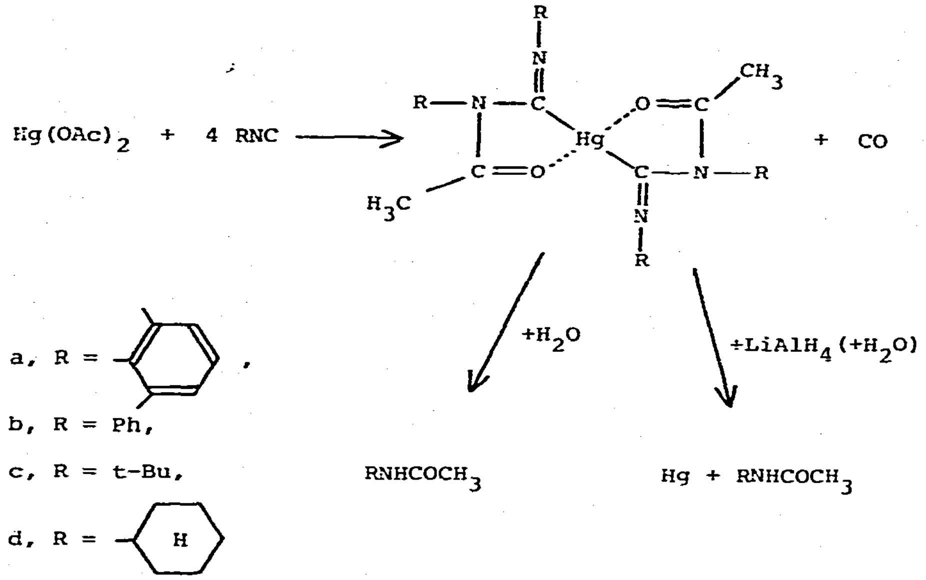


Two possible mechanisms for this reaction were suggested, with the one involving attack by $HgOAc^+$ at the $Me_2C=$ bond being favored:

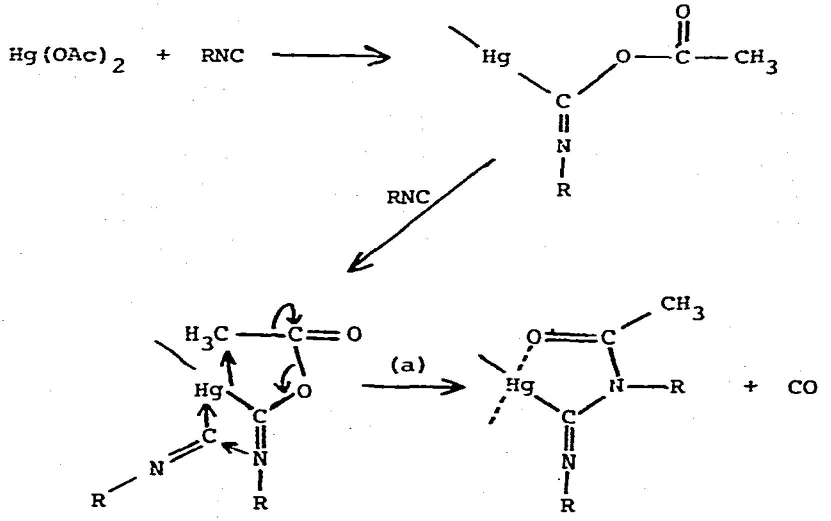


D. Isonitriles

Mercuration of isonitriles with bulky organic substituents gave a novel type of organomercury product whose hydrolysis gave an amide (101):



The structure of the product derived from 2,6-dimethylphenylisonitrile was determined by X-ray crystallography (Fig. 2). The mechanism of formation of these mercurials which was suggested is shown below.



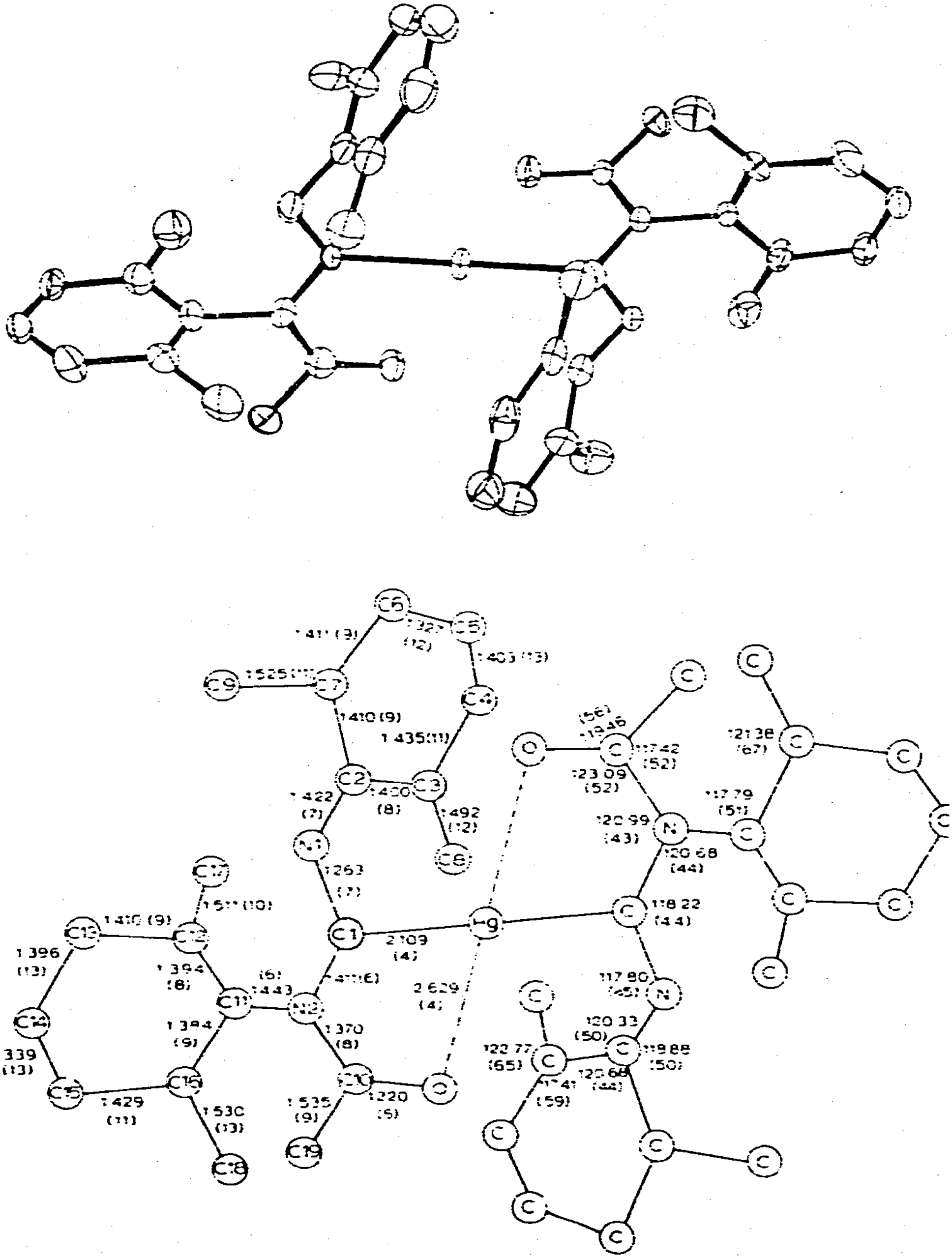
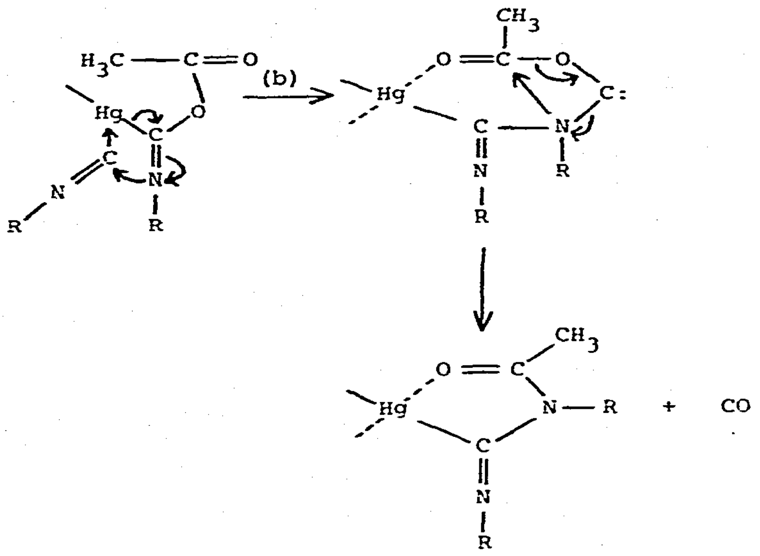
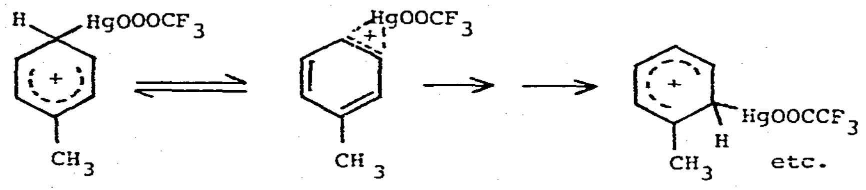


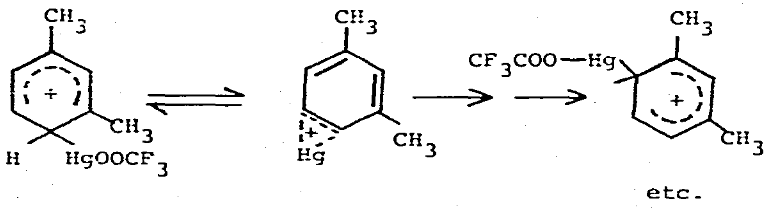
Figure 2. Structure of the organomercury product from the reaction of 2,6-dimethylphenylisonitrile with mercuric acetate. From: H. Sawai, T. Takizawa and Y. Iitaka, J. Organometal. Chem., 120 (1976) 161.



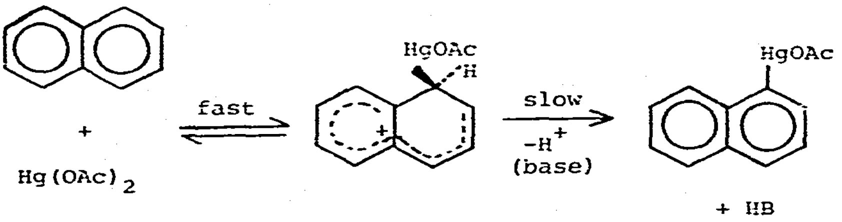
E. Aromatic Compounds

Arenemercurinium ions, the intermediates involved in the mercuration of aromatic compounds, have been studied using proton and ^{13}C NMR spectroscopy by Olah and his coworkers (102). A number of aromatic hydrocarbons (benzene, toluene, anisole, fluorobenzene, m-xylene, p-methylanisole, mesitylene, 1,3,5-trimethoxybenzene and pentamethylbenzene) was mercurated using mercuric trifluoroacetate or methylmercuric acetate with excess fluorosulfuric acid in liquid sulfur dioxide at -78°. The changes in chemical shifts on going from the uncomplexed arenes to the arenemercurinium ions and the J(C-H) coupling observed suggested that the best description of the species present in solution is one involving rapid exchange of σ and π complexes:

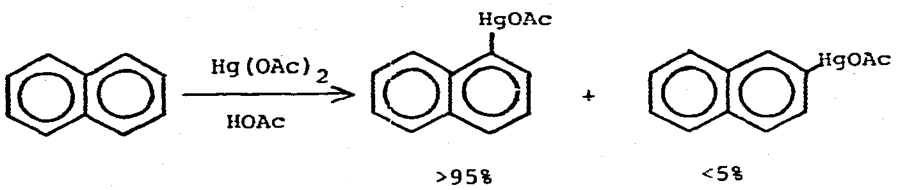




A detailed mechanistic study (kinetics, medium and salt effects, kinetic isotope effects) of the mercuration of naphthalene has been made using mercuric acetate in glacial acetic acid, uncatalyzed, as well as with perchloric acid catalyst (103). It was concluded that a mechanism involving rapid, reversible formation of a σ intermediate in low concentration is followed by rate-determining proton loss:



α-Mercuration was highly favored:



(Continued on p. 236)

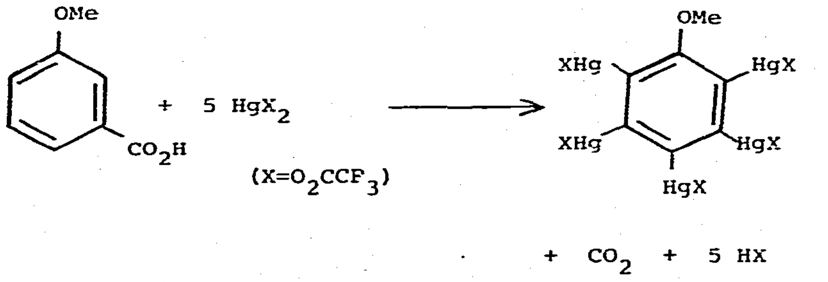
TABLE 12. Polymercuration of Arenes and Brominolysis of the Products. From G. B. Deacon and G. J. Farquharson, Austral. J. Chem., 29 (1976) 627.

Arene	Temp. (°C)	Polymercurated arene	Polybromo-benzene	Yield (%)
$C_6H_5NO_2$	240	$C_6(HgO_2CCF_3)_5NO_2$	$C_6Br_5NO_2$	64
$C_6H_5CO_2Na$	180	$C_6(HgO_2CCF_3)_5CO_2Na$	$C_6Br_5CO_2H$	60
$C_6H_5CO_2H$	180	$C_6(HgO_2CCF_3)_5CO_2H$	$C_6Br_5CO_2H$	57
$C_6H_5CONH_2$	200	$C_6(HgO_2CCF_3)_5CONH_2$	$C_6Br_5CONH_2$	56
$C_6H_5NHCOMe$	200	$C_6(HgO_2CCF_3)_5NHCOMe$	$C_6Br_5NHCOMe$	40
$C_6H_5SO_3Na,2H_2O$	200	$C_6(HgO_2CCF_3)_5SO_3Na$	$(C_6Br_5SO_3)_2Ba$	68
C_6H_5HgCl	180	$C_6H(HgO_2CCF_3)_5$	C_6HBr_5	70
		$+ C_6(HgO_2CCF_3)_6$	$+ C_6Br_6$	7
C_6H_5HgCl	200	$C_6(HgO_2CCF_3)_6$	C_6Br_6	60

TABLE 12 (contd.)

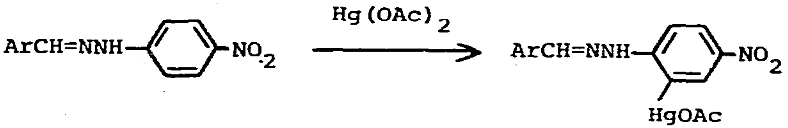
p-$ClC_6H_4CF_3$	245	p-$ClC_6(HgO_2CCF_3)_4CF_3$	p-$ClC_6Br_4CF_3$	61
p-$MeOC_6H_4Me$	180	p-$MeOC_6(HgO_2CCF_3)_4Me$	p-$MeOC_6Br_4Me$	40
$Cl_2C_6H_3F$	210	$CL_2C_6(HgO_2CCF_3)_3F$	$Cl_2C_6Br_3F$	78
p-$MeOC_6H_4CO_2H$	180	$C_6(HgO_2CCF_3)_5OMe$	C_6Br_5OMe	70
p-$MeOC_6H_4CONH_2$	180	p-$MeOC_6(HgO_2CCF_3)_4CONH_2$	p-$MeOC_6Br_4CONH_2$	55
		+ $C_6(HgO_2CCF_3)_5OMe$	+ C_6Br_5OMe	17
p-$MeOC_6H_4CO_2Me$	180	p-$MeOC_6(HgO_2CCF_3)_4CO_2Me$	p-$MeOC_6Br_4CO_2Me$	62
		+ $C_6(HgO_2CCF_3)_5OMe$	+ C_6Br_5OMe	7

Of special interest is the synthesis of permercurated arenes by Deacon and Farquharson (104) using the reaction of arenes with molten mercuric trifluoroacetate at 180-245°. Brominolysis with Br_2/KBr of the products proved to be a good route to perbromoarenes. The results of this study are summarized in Table 12. The permercuration of p-methoxybenzoic acid (but not of benzoic acid itself) proceeded with decarboxylation:



The mercuration of phenols by mercuric acetate in glacial acetic acid at 90° proceeds in better yield when a few drops of 40% hydrofluoric acid are added (105). *o*-, *m*- and *p*-Cresyl alkyl ethers have been mercurated with mercuric acetate (106), as have silylated ethers of type $R_3Si(CH_2)_nOC_6H_4R'$ (R = alkyl, aryl; R' = H, Me, MeO; n = 1,3) (107).

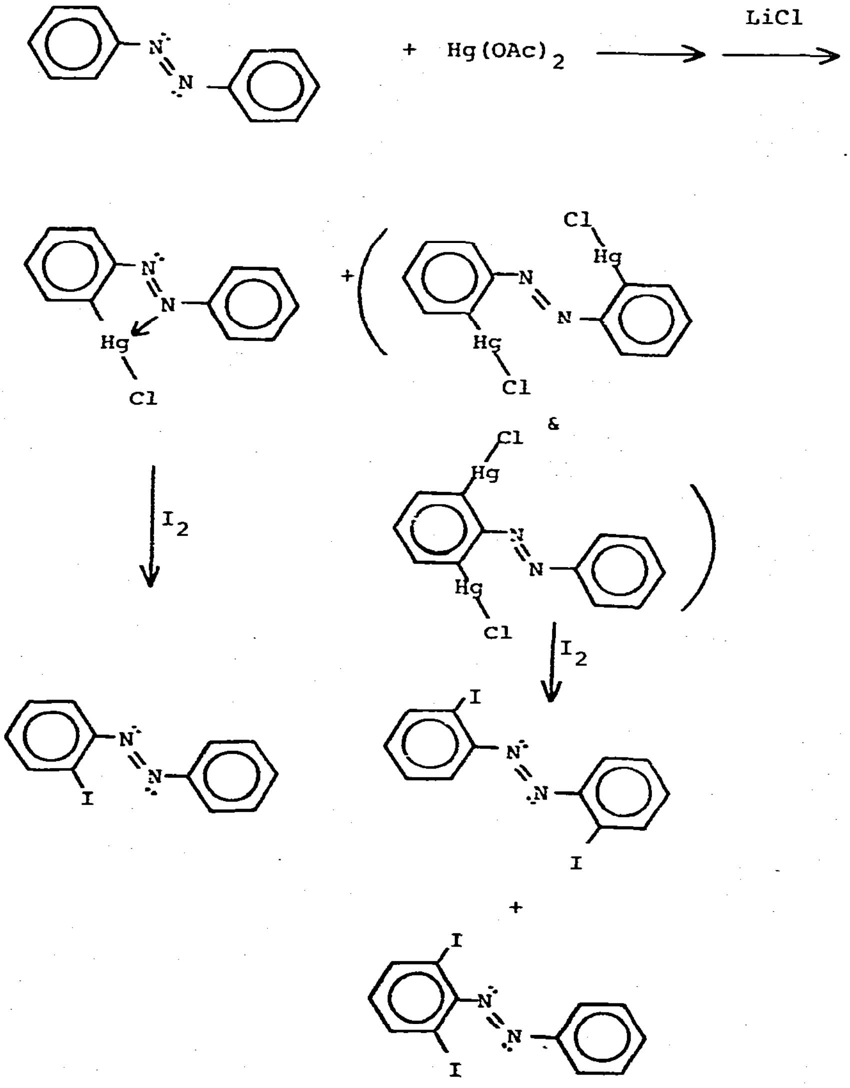
Full details have been reported concerning the mercuration of azobenzene and *ortho*-substituted azobenzenes (108) (Scheme 1). The results are shown in Table 13. *ortho*-Mercuration clearly is preferred, which suggests that coordination of the attacking mercury reagent to an azo nitrogen is an important feature of the reaction course (Scheme 2). Further evidence for such complex formation before and during the rate-determining step of the mercuration was provided by a kinetic study of the reaction of mercuric acetate with 2-methylazobenzene in methanol (109). *ortho*-Mercuration also was observed in the reaction of mercuric acetate with some arylhydrazones (110):



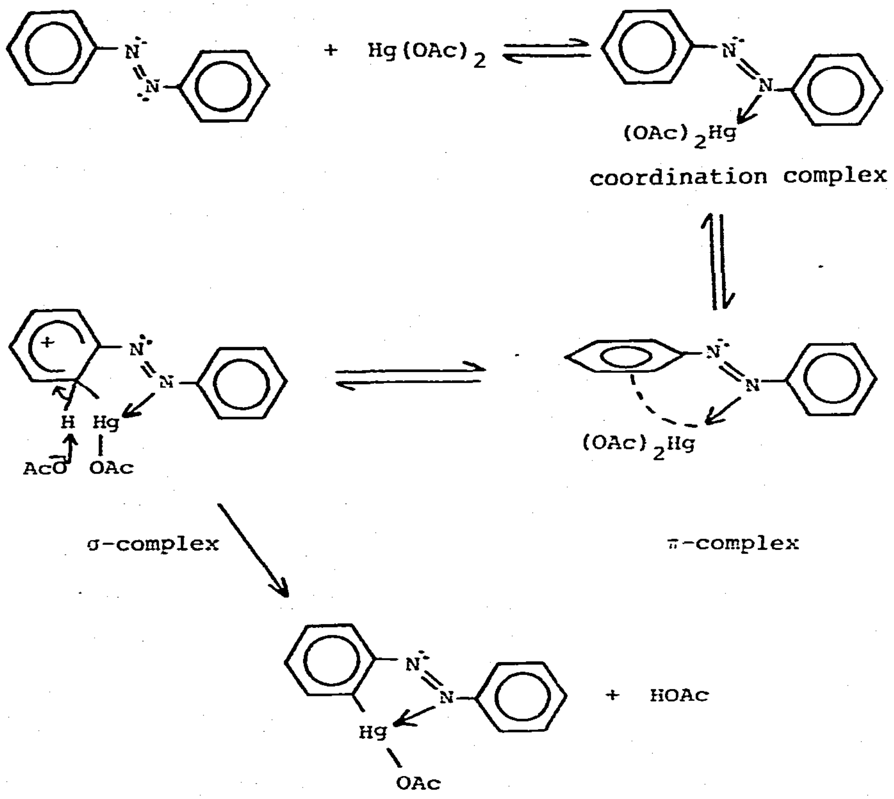
$(Ar = C_6H_5,\ p\text{-}MeC_6H_4,$

$p\text{-}ClC_6H_4)$

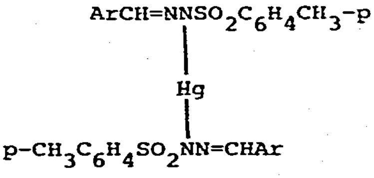
SCHEME 1



SCHEME 2



p-Tolylsulfonylhydrazones, on the other hand, formed N-mercury derivatives of type 24. Both types of hydrazones reacted with phenylmercuric acetate to form N-phenylmercury derivatives.



$$\begin{array}{c} \mathrm{ArCH{=}NNSO_2C_6H_4CH_3\text{-}p} \\ | \\ \mathrm{Hg} \\ | \\ \mathrm{p\text{-}CH_3C_6H_4SO_2NN{=}CHAr} \end{array}$$

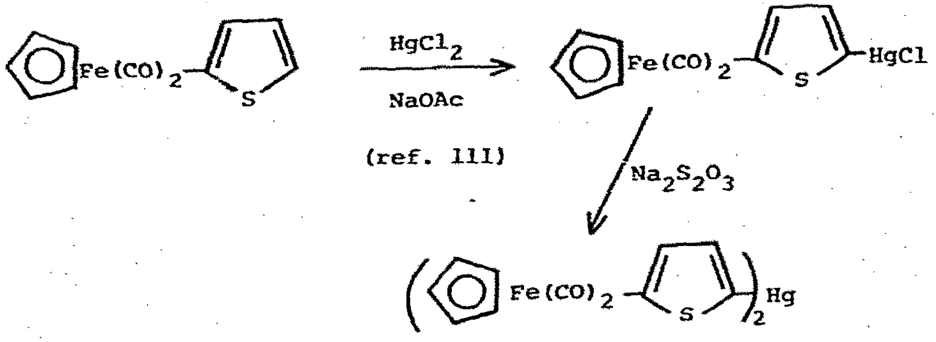
24

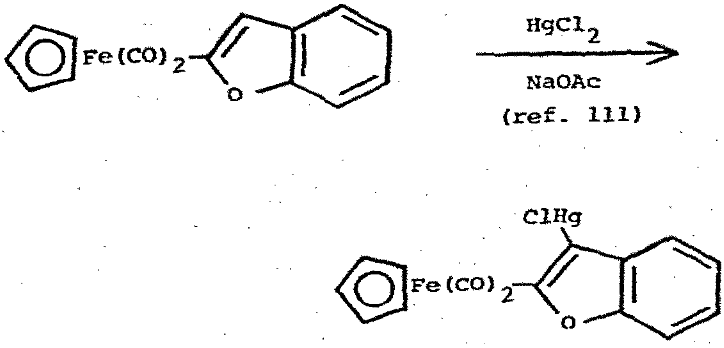
TABLE 13. Mercuration of Azobenzenes.[a] From P. V. Roling et al., J. Org. Chem. 116 (1976) 39.

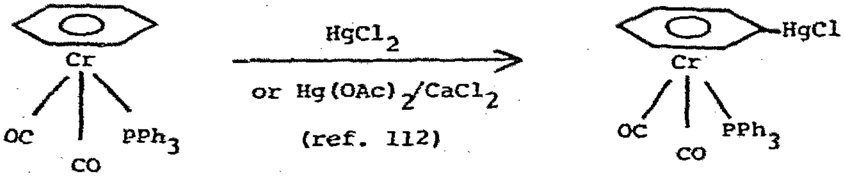
Starting azobenzene				Yield[b] of products (%)					
Substituents			Recovery (%)	Monomercurials Substitution position		Dimercurials Substitution positions			Total
O	O	O'		O	O'	O,O'	O',O'	Other	
--	--	--	40	40	--	3	3	0	46
CH_3	--	--	20	71	0	0	0	0	71
CH_3	--	CH_3	39	51	--	4	--	0	55
CH_3	CH_3	--	72	--	10	--			
CH_3O	--	--	24	0	63	1	4	1	69
CH_3O	--	CH_3O	27	54	--	10	--	0	64
i-PrO	--	--	35	24					
I	--	--	70	20	2	0	0	0	22
Cl	--	--	75	13	7	0	0	0	20
NO_2	--	--	93	5	1	0	0	0	6
CN	--	--	96	1	0	0	0	0	1

[a] The results listed here are for the equimolar reaction of an azobenzene and mercuric acetate in refluxing methanol for 22 h. [b] The % yields are based on the azobenzene. The dimercurials, except for that of 2,2'-dimethylazobenzene, were not isolated.

The mercuration of some organotransition metal compounds also has been described by Russian workers.







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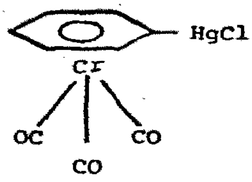
All attempts to symmetrize 25 and 26 failed (112).

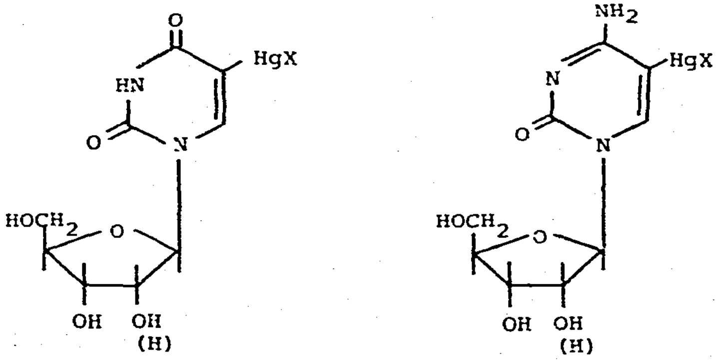


26

Benzenechromium tricarbonyl was found to react with mercuric chloride not to give the arene mercuration product 26, but rather $(C_6H_6)Cr(CO)_3 \cdot nHgCl_2$ adducts (n = 2,3) in which the chromium atom was assumed to be the donor site (112, 113).

5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

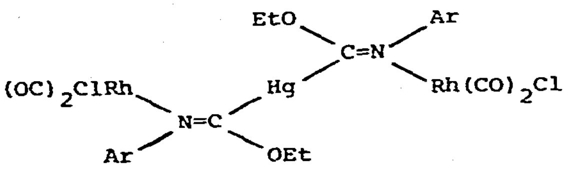
Mercurated nucleotides of cytosine and uracil and of polynucleotides are readily prepared by direct mercuration in buffered aqueous medium. Typical products are:



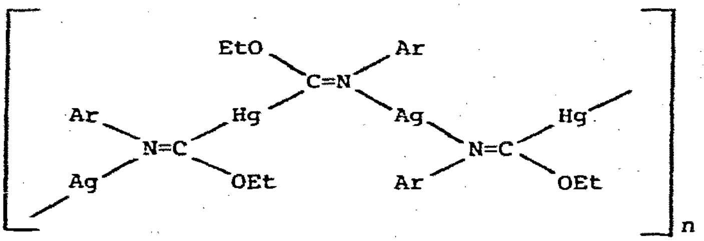
Structure of 5-mercuriuridine (deoxyuridine), and 5-mercuricytidine (deoxycytidine). The mercury ligand, X, may be Cl^-, CN^-, R-S^-, or other appropriate counterion.

Such mercurials are stable under physiological conditions and show promise of diverse useful applications in biochemical investigations (114, 115, 44).

The novel isonitrile-derived mercurial $Hg[C(OEt)=N$-$C_6H_4CH_3$-$p]_2$ can function as a ligand in transition metal complexes (116), e.g.:



and the polymeric

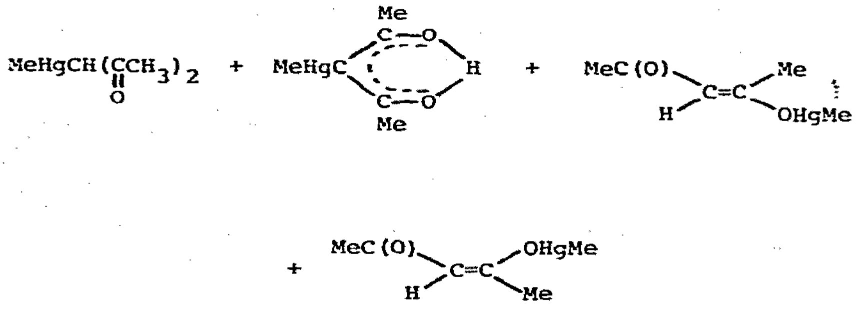


The mercurial-ligand itself forms a dipicrate salt.

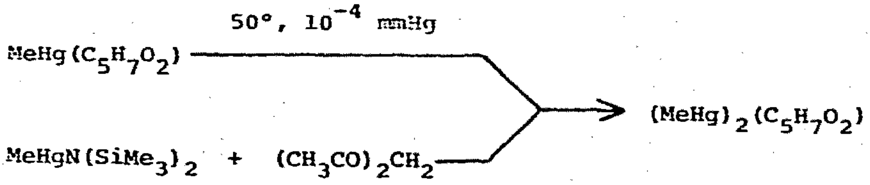
Further work has been carried out on organomercury-diketone compounds, with Clare and Glockling investigating compounds of types MeHg(diketone), $(MeHg)_2$(diketone) and MeHg(amine)(diketone) (117):

$$MeHgN(SiMe_3)_2 + (CH_3CO)_2CH_2 \xrightarrow{Et_2O} \text{"}MeHg(C_5H_7O_2)\text{"}$$

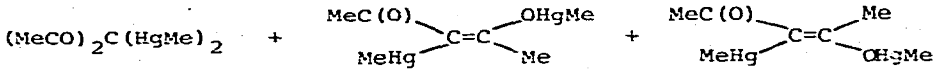
The product, according to its proton NMR spectrum, is a mixture of Hg-C and Hg-O bonded species:

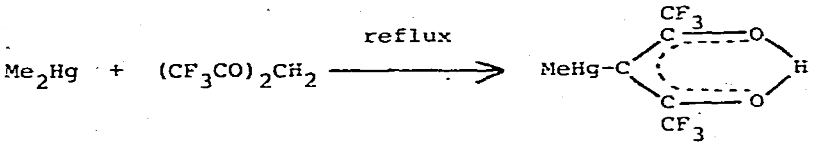


A bis-mercurated compound also was prepared:



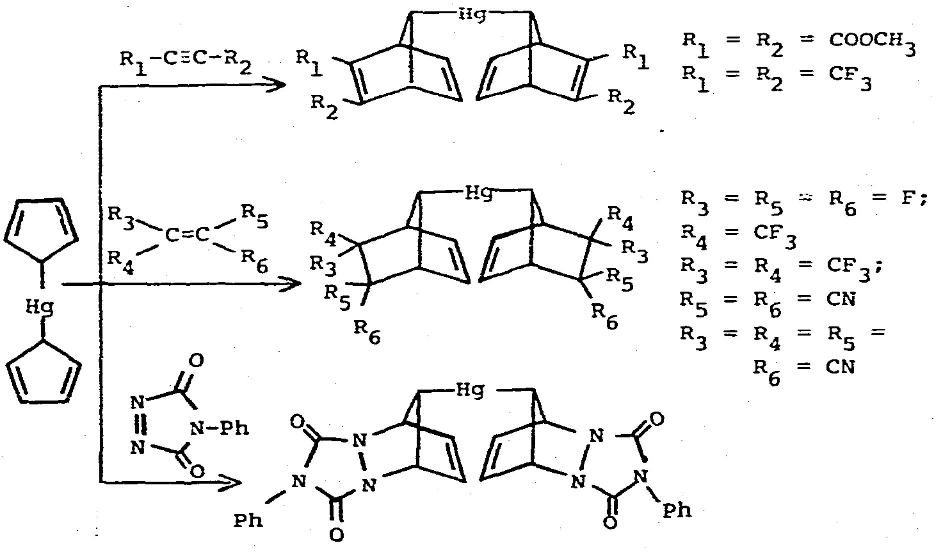
This product appears to be a mixture of three species:





This fluorine-containing product formed 1:1 complexes with ammonia and amines. Polish workers have studied "dimercurymalonic acid", a material which precipitates when stoichiometric amounts of mercuric nitrate and malonic acid are mixed. The given composition, $HgC(CO_2)_2Hg$, brings no structural information (118).

Stone and his coworkers have prepared organofunctional mercurials by Diels-Alder reactions of dicyclopentadienylmercury with activated acetylenes ($MeO_2CC{\equiv}CCO_2Me$, $CF_3C{\equiv}CCF_3$), olefins ($CF_3CF{=}CFCF_3$, $CF_3CF{=}CF_2$, $(CF_3)_2C{=}(CN)_2$, $(NC)_2C{=}C(CN)_2$) and 4-phenyl-1,2,4-triazoline-3,5-dione (119):

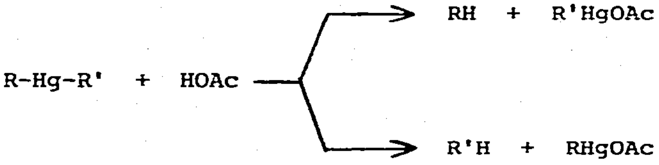


$R_1 = R_2 = COOCH_3$
$R_1 = R_2 = CF_3$

$R_3 = R_5 = R_6 = F$; $R_4 = CF_3$
$R_3 = R_4 = CF_3$; $R_5 = R_6 = CN$
$R_3 = R_4 = R_5 = R_6 = CN$

6. MERCURY-CARBON BOND REACTIONS

The electrophilic cleavage of the mercury-carbon bond has been studied in great detail by many research groups throughout the world since the early work of Kharasch in the 1920s on this subject. Nugent and Kochi have attacked this problem anew and have carried out a study of the acetolysis of pure, unsymmetrical dialkylmercury compounds using glacial acetic acid under argon at 37.5° and following the reaction rates by gas chromatographic analysis of the gaseous paraffin hydrocarbons which were formed (120). The pseudo-



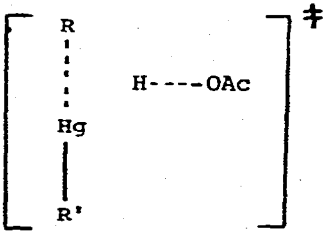
first order rate constants thus determined are shown in Table 14. (The rates for the symmetrical mercurials are statistically corrected). The rates of cleavage of the t-butyl groups were too slow for direct measurement by the GLC procedure, and the behavior of di-t-butylmercury was quite different: An initial slow rate was observed, followed by rapid decomposition to isobutylene and elemental mercury , in addition to formation of isobutane. This study showed the operation of both leaving group (HgR') effects and cleaved alkyl group (R) effects, and these are shown schematically in Chart 1, with the numerical values given = 7 + log k and 7 + log k' (see Table 14). The logarithms of these pseudo-first order rate constants for RHg-CH_3 cleavage correlated linearly with the gas phase ionization potentials (as determined by He I photoelectron spectroscopy) of $RHgCH_3$. Thus the effect of the leaving group RHg^+ on the rate of cleavage of the RHg-CH_3 bond by acetic acid provides good indication of the ability of the alkyl group R to delocalize positive charge in the transition state under conditions in which the RHg moiety remains intact. Large kinetic isotope effects (9-11) were found. On the basis of the present work and the previously established retention of stereochemistry at carbon in such C-Hg bond protolysis, the authors suggested that the three center transition state <u>27</u> is operative. The

TABLE 14. Acetolysis of Unsymmetrical Dialkylmercury Compounds: Pseudo-First Order Rate Constants. From W. A. Nugent and J. K. Kochi, J. Amer. Chem. Soc., 98 (1976) 5979.

R-Hg-R'		Cleavage of R	Cleavage of R'
R	R'	10^7k (s^{-1})	$10^7k'$ (s^{-1})
Me	Me	3.90	3.90
Me	Et	23.5	14.3
Me	i-Pr	85.8	8.45
Me	t-Bu	120	-
Et	Et	81.8	81.8
Et	i-Pr	255	47.0
Et	t-Bu	378	-
i-Pr	i-Pr	154	154
i-Pr	t-Bu	224	ca. 10

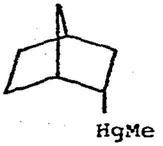
CHART 1 Leaving Group and Cleaved Group Effects of Alkyl Ligands in the Protonolysis of Organomercurial.

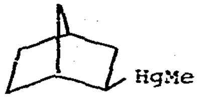
		LEAVING GROUP			
		HgMe	HgEt	HgPr^i	HgBu^t
CLEAVED GROUP	Me	0.59	1.37	1.93	2.08
	Et	1.16	1.91	2.41	2.58
	i-Pr	0.93	1.67	2.19	2.35



27

question of nucleophilic assistance was not addressed in this study. All the acetolysis rates are correlated by the equation $\log k/k_o = L + C$, where L is the leaving group constant for *HgR', which is determined only by an electronic effect, and* C is the cleaved group constant for R. This work was extended to a study of the cleavage of compounds <u>28</u> and <u>29</u> (121). The larger value for the rate of cleavage for the Me-Hg bond

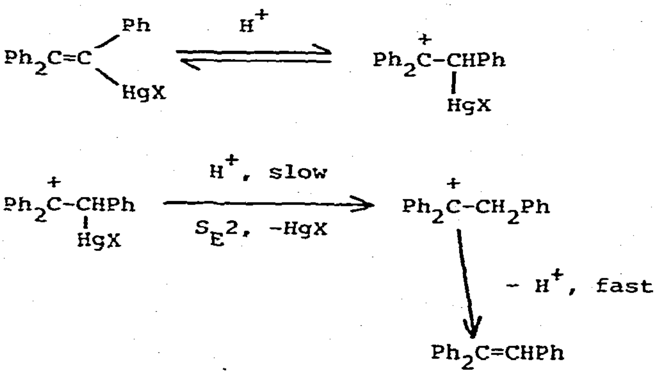




<u>28</u> $10^7k\ (s^{-1}) = 66.5$ <u>29</u> $10^7k\ (s^{-1}) = 86.3$

of the <u>exo</u> isomer is further evidence for σ participation in the transition state.

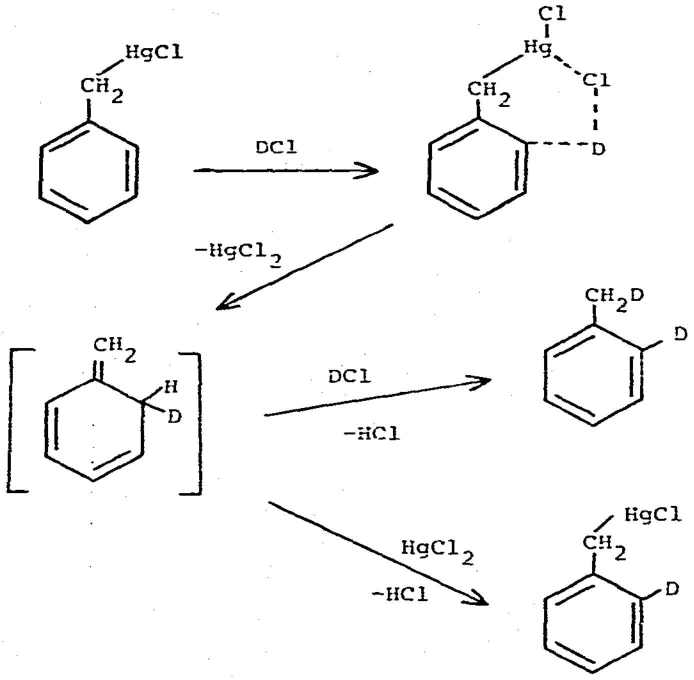
The solvolysis of triphenylvinylmercuric acetate or bromide in acetic acid in the presence of perchloric acid gave triphenylethylene rather than the triphenylvinyl cation-derived $Ph_2C{=}C(Ph)OAc$ (122). Kinetic studies suggested the following mechanism:



$$Ph_2C{=}C\genfrac{}{}{0pt}{}{Ph}{HgX} \xrightleftharpoons{H^+} Ph_2\overset{+}{C}{-}\underset{HgX}{C}HPh$$

$$Ph_2\overset{+}{C}{-}\underset{HgX}{C}HPh \xrightarrow[S_E2,\ -HgX]{H^+,\ slow} Ph_2\overset{+}{C}{-}CH_2Ph \xrightarrow{-H^+,\ fast} Ph_2C{=}CHPh$$

The mechanism of the reaction of benzylmercurials with DCl in which deuterium is incorporated into the <u>ortho</u> and <u>para</u> positions of the aromatic ring has received further experimental study (123). It was found that the rate of deuteriodemetalation of $PhCH_2HgCl$ and the isotope enrichment rate of the mercurial are markedly dependent on the concentration of added mercuric chloride. A two-step mechanism involving intermediate C-Hg bond cleavage was suggested in place of the previously favored mechanism involving C-Hg bond hyperconjugative interaction:



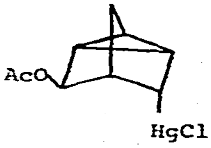
Mercury-carbon bond cleavage by halogens and related reagents also has received further attention. The reaction of cis-PhCH=CHHgCl with chlorine, bromine and iodine in acetic acid solution in the dark at room temperature is almost completely stereospecific (Table 15) (124). On the other hand, halogenolysis of the corresponding trans isomers is slower and significantly less stereospecific. A radical process was suggested. The cleavage of dibenzyl- and diphenylmercury and trans-4-methylcyclohexylmercuric bromide by bromine in toluene or in p-fluorotoluene in the dark proceeded with concommitant benzylic bromination of the solvent (125). This process was suppressed by addition of hydroquinone. Operation, in part, of a radical mechanism was suggested. Second-order kinetics were found for the cleavage of o-chloromercuriphenol by iodine in various al-

TABLE 15. Stereochemistry of Halogenolysis of β-Styrylmercuric Halides. (From D. Dodd, M. D. Johnson, B. S. Meeks, D. M. Titchmarsh, K. N. Van Duong and A. Gaudemer, J. Chem. Soc., Perkin Trans. II (1976) 1261).

PhCH=CHHgX		PhCH=CHX (% Yield)	
Isomer	X=	trans	cis
cis	Cl	95	5
cis	Br	98	2
cis	I	99	1
trans	Cl	10	90
trans	Br	12	88
trans	I	10	90

cohols (126) and by ICl_3 in acetic acid (127).

The cleavage of erythro- and threo-3,3-dimethyl-1,2-d_2-butylmercuric chloride and of 30 and 31 by copper(II) bromide in chloroform or benzene proceeded with loss of stereochemistry at carbon (128). This speaks for a radical process rather than a concerted cleavage mechanism. Organocopper intermediates possibly are involved:



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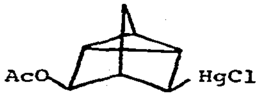


31

$$RHgCl + CuBr_2 \longrightarrow RCuBr + HgClBr$$

$$RCuBr \xrightarrow{\text{fast}} R\cdot + CuBr$$

$$R\cdot + CuBr_2 \xrightarrow{\text{fast}} RBr + CuBr$$

An electron transfer process is involved in the dealkylation of dialkylmercurials by $Na_2IrCl_6 \cdot 6H_2O$ (129):

$$R_2Hg \; + \; IrCl_6^{2-} \xrightarrow{k} R_2Hg^{\cdot +} \; + \; IrCl_6^{3-}$$

$$R_2Hg^{\cdot +} \xrightarrow{\text{fast}} RHg^{+} \; + \; R^{\cdot}$$

$$R^{\cdot} \; + \; IrCl_6^{2-} \xrightarrow{\text{fast}} R_{ox} \; + \; IrCl_6X^{n-}$$

(X = solvent; n = 2
X = Cl^-; n = 3)

In the case of dimethyl- and diethylmercury the organic products were the alkyl chlorides, but in the case of diisopropyl- and di-tert-butylmercury, olefinic products were formed. Evidence for intermediate alkyl radicals was obtained by spin trapping and oxygen scavenging experiments. The RHg^+ residue (see Scheme above) appears to be trapped by the reduced chloroiridium(III) species, giving a binuclear complex of type $RHgClIrCl_4(CH_3CN)^{-1}$ when the reaction is carried out in acetonitrile. The log k values for these cleavage reactions were found to correlate well with vertical ionization potentials and the frequencies of the CT bands of R_2Hg/tetracyanoethylene complexes, which provides good evidence that an electron transfer process is involved, i.e., $R_2Hg \longrightarrow R_2Hg^{\cdot +} + e^-$.

Nugent and Kochi have studied further free radical reactions of organomercurials. The use of suitable unsymmetrical dialkylmercurials allowed a better study of the reductive elimination reaction of R_2Hg compounds with carbon tetrachloride (130):

$$CCl_4 \longrightarrow \cdot CCl_3$$

$$HCMe_2CH_2HgR \; + \; \cdot CCl_3 \longrightarrow \cdot CMe_2CH_2HgR \; + \; HCCl_3$$

($R = Me_3CCH_2$)

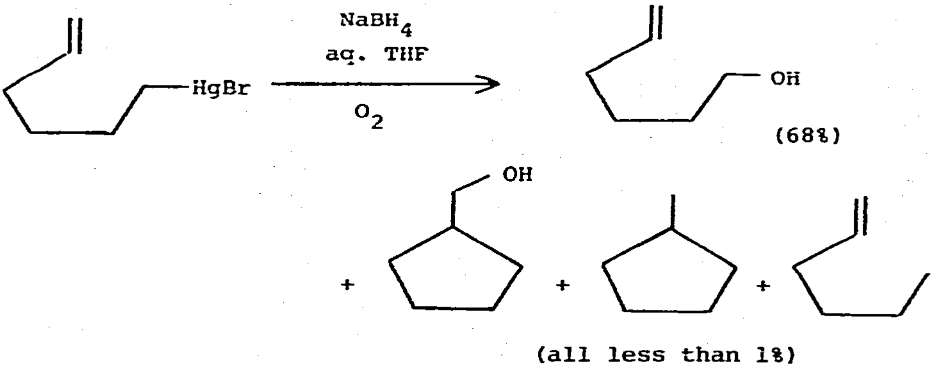
$$\cdot CMe_2CH_2HgR \longrightarrow Me_2C{=}CH_2 \; + \; RHg^{\cdot}$$

$$RHg^{\cdot} \longrightarrow Hg^{\circ} \; + \; R\cdot$$

$$R\cdot \quad + \quad CCl_4 \longrightarrow RCl \quad + \quad \cdot CCl_3$$

This H atom abstraction process is accelerated by β mercury over similar abstraction in cyclohexane by a factor of 600, and the reactions proceed more rapidly in the presence of butyryl peroxide and are inhibited by galvinoxyl. In the reaction of "mercuracycloheptane" with carbon tetrachloride, formation of cyclopentylmethyl chloride as well as of 6-chlorocyclohexene provided additional evidence for a radical mechanism. Russian workers have studied the effect of added tetrahydrofuran on the R_2Hg/CCl_4 reaction and found that it has a rate-accelerating effect (131). It was suggested that an initial R_2Hg/THF complex is formed which is more reactive toward CCl_4 than is R_2Hg by itself. Unfortunately, experimental details concerning mercurial, carbon tetrachloride and THF purification, degassing procedures and reaction conditions were not provided, so it is impossible to evaluate these results which depend so critically on these factors.

Other radical processes involving organomercurials have been studied. Further evidence has been provided that the reduction of organomercuric halides by $NaBH_4$, $LiAlH_4$ and n-Bu_3SnH is a process involving non-caged, free radical intermediates. Thus the reduction of $CH_2{=}CH(CH_2)_4HgBr$ by these hydrides gave 1-hexene and methylcyclopentane (132). This is a clear indication that the hex-5-enyl radical was formed since this species is known to undergo ready cyclization. When the reduction of $CH_2{=}CH(CH_2)_4HgBr$ by $NaBH_4$ was carried out in aqueous THF in the presence of molecular oxygen, the results shown in the equation below were obtained:



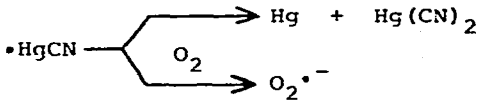
Apparently the trapping of the hex-5-enyl radicals by O_2 is faster than the cyclization reaction. In accord with the fact that sodium amalgam reduction of RHgX compounds is not a radical process, the reduction of $CH_2{=}CH(CH_2)_4HgBr$ by this reagent gave only 1-hexene. As the authors point out, in RHgX systems where intermediate radicals are prone to rearrangement, Na/Hg thus is the reducing agent of choice for use in carbon skeleton structure proof, D-labelling and synthesis.

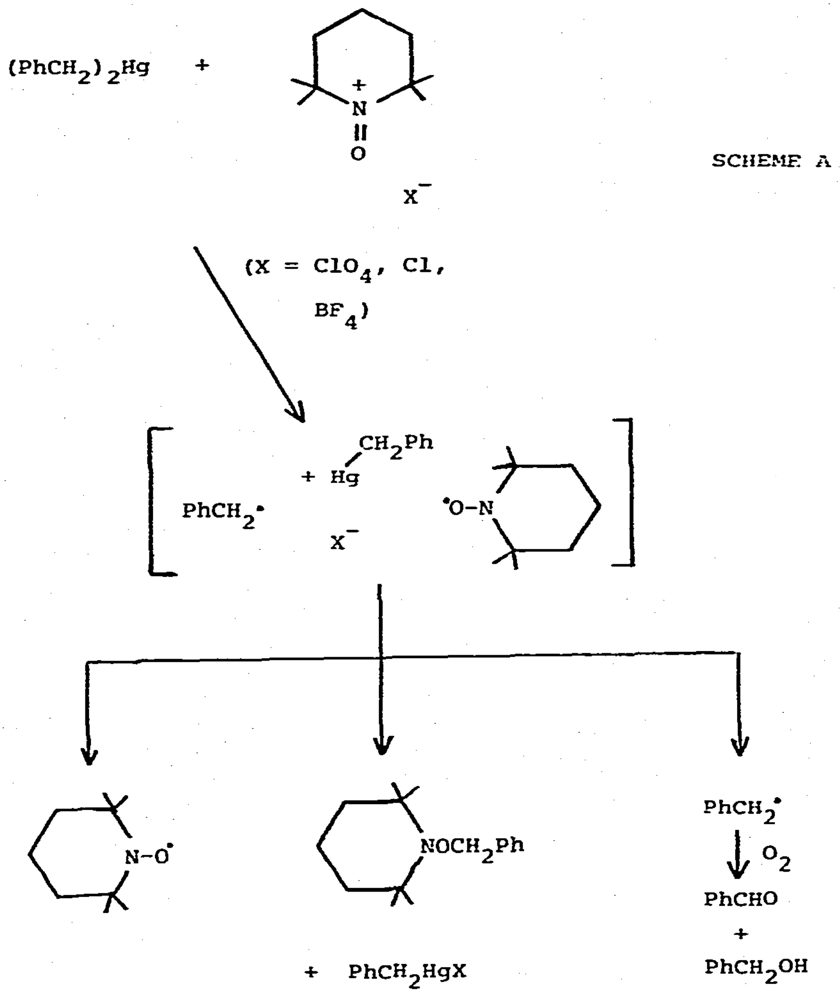
Radicals also were formed in the reactions of 2,2,6,6-tetramethyl-1-oxopiperidinium salts with dibenzylmercury and the *cis* and *trans* isomers of 4-methylcyclohexylmercuric bromide (133). The latter reacted with loss of stereochemistry at carbon and, also, in the case of dibenzylmercury, benzaldehyde and benzyl alcohol, as well as the nitroxyl radical were formed (SCHEME A).

CIDNP studies of the photolysis of symmetrical and unsymmetrical diorganomercurials provided no evidence for the formation of free radicals of type $RHg^\bullet$. Product formation can take place *via* free $R^\bullet$ radicals or by processes involving singlet or triplet R_2Hg excited states, depending on the solvent used (134). A pulsed FT NMR ^1H-CIDNP study of the photolysis and thermolysis of di-tert-butylmercury showed these to be radical processes which occur in a cage reaction (135).

The absorption spectra of dialkylmercurials show charge transfer bands in the presence of tetracyanoethylene (TCNE). Ultimately, TCNE inserted into the C-Hg bond, giving $RHg{-}C(CN)_2C(CN)_2R$, at rates that were dependent on R (*i*-Pr > *n*-alkyl > methyl) (136). Analogous reactions with tetraalkyllead compounds were shown to proceed by an electron transfer mechanism, so it is likely that this is the case also for the R_2Hg compounds.

The transient radical .HgCN was obtained by reduction of mercuric cyanide in aqueous solution by hydrated electrons and was characterized by its optical absorption spectrum. Based on the latter and its chemical behavior:





SCHEME A

a 3-electron bond between Hg and CN, $\text{Hg} \therefore \text{CN}$, was suggested, with the third electron in a σ^* orbital (137).

Further miscellaneous reactions involving the mercury-carbon bond may be mentioned:

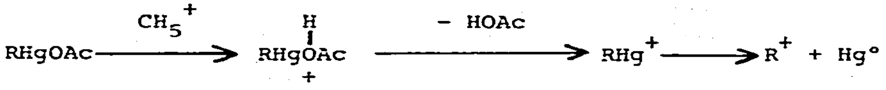
Reutov et al. have determined the kinetic isotope effect in the reaction of diisobutylmercury with $Ph_3C^+ClO_4^-$ in 1,2-dichloroethane as k_H/k_D (βH) = 4.2 (138). It would seem that the rate-limiting step involves β C-H bond rupture of the dialkylmercury compound:

$$(Me_2CHCH_2)_2Hg + Ph_3C^+ClO_4^- \longrightarrow Me_2C{=}CH_2 + Ph_3CH + Me_2CHCH_2HgClO_4$$

Pulse radiolysis of dibenzylmercury in solution generates the benzyl carbonium ion (139):

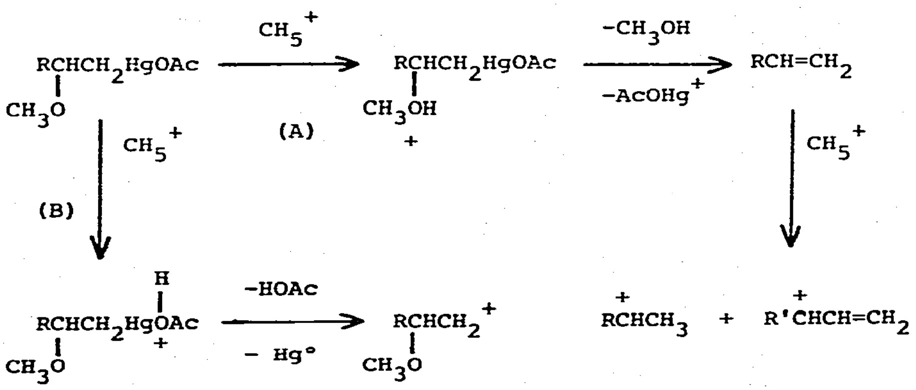
$$(PhCH_2)_2Hg \xrightarrow[\text{pulse radiolysis}]{ClCH_2CH_2Cl} PhCH_2^+$$

Rates of reaction of the carbocation with various nucleophiles (X^-, R_3N, ROH) were studied. Finally, reactions of organomercurials in the gas phase have been examined using chemical ionization mass spectroscopy (140). Organomercuric cations were formed from RHgOAc compounds, which then underwent demercuration to give carbonium ions:



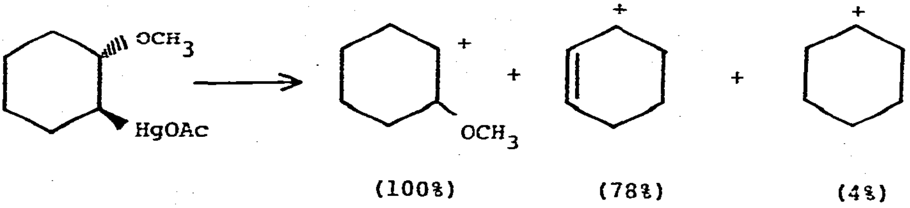
$$RHgOAc \xrightarrow{CH_5^+} RHg\overset{H}{O}Ac^+ \xrightarrow{-\,HOAc} RHg^+ \longrightarrow R^+ + Hg^\circ$$

In some cases (R = Me, Ph), the RHg^+ cation could be detected, but with other alkylmercuric acetates, only the carbonium ion was detectable. β-Alkoxyalkylmercurials underwent both demercuration and deoxymercuration:



R	% Demercuration (B)	% Deoxymercuration (A)	B/A
Ph	96	4	24
CH_3CH_2	76	24	3.2
$CH_3(CH_2)_6$	59	41	1.4

and



7. MERCURY-FUNCTIONAL MERCURIALS

A. Mercurials with Halogen, Pseudohalogen, Oxygen, Sulfur, Selenium and Nitrogen Substituents.

Proton NMR and Raman spectroscopy have been used to study the complexation of $CH_3Hg(II)$ by SO_4^{2-}, SeO_4^{2-}, CO_3^{2-}, SO_3^{2-} SCN^-, $SeCN^-$, S^{2-} and Se^{2-} in aqueous solution (141). Ligand donor atoms were determined (e.g., S or O in SO_3^{2-}) and formation constants, K_f, as defined below, were determined (Table 16).

$$MeHg^+ + L^{n-} \rightleftharpoons MeHgL^{(n+1)-}$$

$$K_f = \frac{[MeHgL^{(n+1)-}]}{[MeHg^+][L^{n-}]}$$

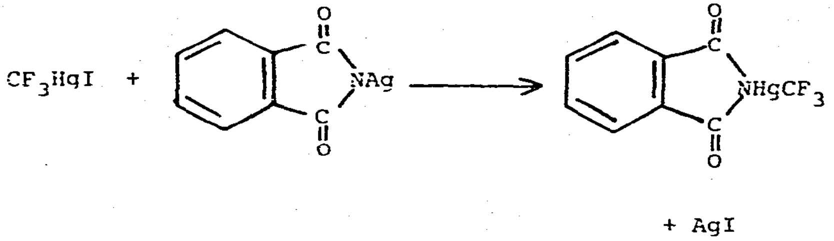
A series of CF_3HgY (Y = CN, NCO, SCN, SeCN, N_3, SCF_3, IO_3) and $(CF_3Hg)_2Z$ (Z = O, C_2O_4, NCN) compounds has been prepared by silver salt metathesis with CF_3HgI (142). Other preparations carried out in this study included:

$$2\ CF_3HgI + Tl_2CS_3 \longrightarrow (CF_3Hg)_2S + CS_2 + 2\ TlI$$

$$(CF_3Hg)_2O + H_2Se \longrightarrow (CF_3Hg)_2Se + H_2O$$

$$2CF_3HgI + (AgNH)_2SO_2 \longrightarrow (CF_3HgNH)_2SO_2 + 2\ AgI$$

$$2\ CF_3HgI + (AgNSCF_3)_2SO_2 \longrightarrow (CF_3HgNSCF_3)_2SO_2 + 2\ AgI$$



$$2\ CF_3HgI + CF_3SO_2NAg_2{\cdot}NH_3 \longrightarrow CF_3SO_2N(HgCF_3)_2\ .$$

The selenide is rather unstable:

$$(CF_3Hg)_2Se \xrightarrow{50°} (CF_3)_2Hg + HgSe$$

Organomercury derivatives of phenols exchange with free phenols (143):

$$PhHgOAr + Ar'OH \rightleftharpoons PhHgOAr' + ArOH$$

Such equilibria have been studied using IR spectroscopy. The equilibrium constants for such exchanges, in which PhHg-$OC_6H_4NO_2$-p was the reference compound, depend on polar substituent effects, with electron-withdrawing substituents favoring the formation of the PhHg derivative of the phenol.

The thermal decomposition of the relatively stable organomercury peroxides, $RHgOOCMe_2Ph$ (with R = Et, i-Pr, Ph, p-ClC_6H_4, p-$MeOC_6H_4$) and $PhHgOOCMe_3$, in toluene and in nonane solution proceeded at an appreciable rate only above 100°. A product and kinetic study suggested that a radical process

TABLE 16. Formation Constants of Methylmercury Complexes.[a] (From D. L. Rabenstein, M. C. Tourangeau and C. A. Evans, Can. J. Chem., 54 (1976) 2517.

Ligand	Donor atom	$[CH_3Hg(II)]_{total}$	$[Ligand]_{total}$	pH range	log K_f
SO_4^{2-}	O	0.0532 M	0.213 M	1.5-5.5	0.94±0.02
SeO_4^{2-}	O	0.0521	0.208	1.5-6	1.12±0.02
CO_3^{2-}	O	0.190	0.380	8-12	6.10±0.10
SO_3^{2-}	S	0.0546,0.0617	0.546,0.0617	9.5-12	7.96±0.02
SeO_3^{2-}	O	0.112	0.224	7-11.5	6.46±0.02
SeO_3H^-	O	0.112	0.224	1-6	2.70±0.05
SCN^-	S	0.05	0.13	8.5-10.5	6.05±0.01
$SeCN^-$	Se	0.06	0.015	8.5-9.5	6.79±0.01

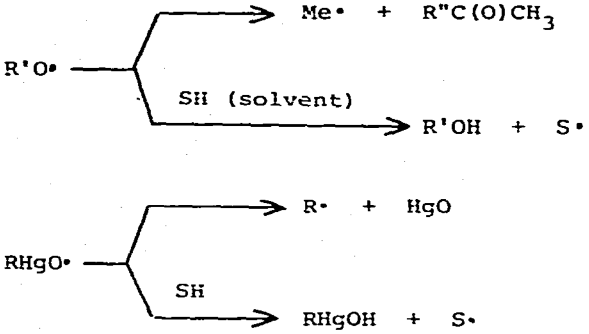
---

[a] Concentration constants at 25°C. Uncertainties are the standard deviations of from four to ten values.

was operative (144):

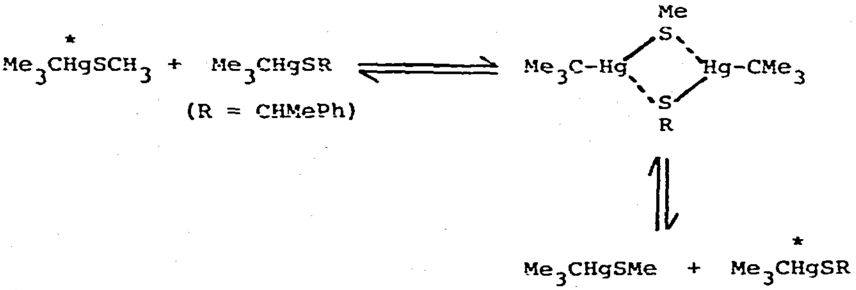
$$\mathrm{RHgOCR'} \xrightarrow{\qquad} \mathrm{RHgO\bullet} + \mathrm{R'O\bullet}$$

$(R' = CMe_2Ph)$



$$2\ \mathrm{RHgOH} \xrightarrow{\qquad} \mathrm{R_2Hg} + \mathrm{HgO} + \mathrm{H_2O}$$

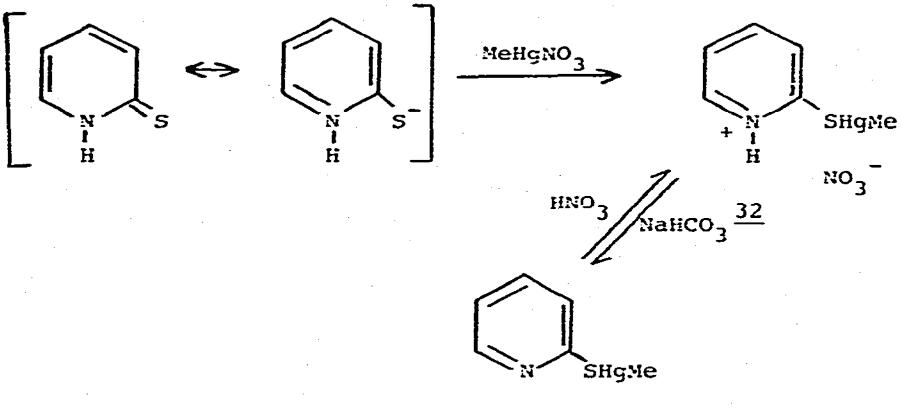
A number of studies have dealt with organomercury-sulfur compounds. Bach and Weibel studied anion exchange reactions of alkylmercury mercaptides by NMR spectroscopy (145). A bimolecular mechanism which involves bridged, not ionic, intermediates was established, e.g.,



The rate of anion exchange was found to parallel the bridging capacity of the substituent on mercury. Anion exchange reactions of methylmercuric cyanide with CH_3HgY (Y = Cl, OAc, Br, SCN, SMe, SPh, SC_6H_4Cl-p and SMe_3) also proceeded <u>via</u> a four-center, bridged intermediate, with the rates of exchange increasing in the order given.

Methylmercuric nitrate was found to react with pyridine-

2(1H)-thione in acetone to give 32, whose treatment with sodium bicarbonate gave 33 (146).



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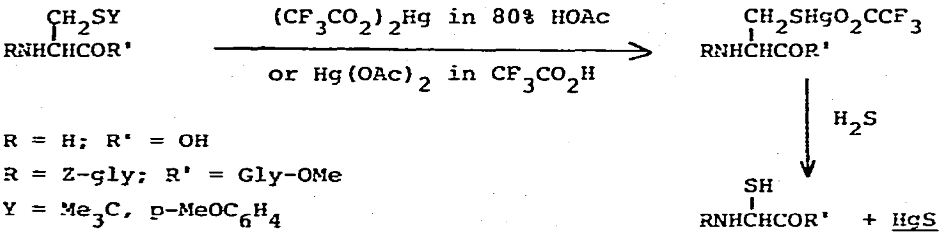
S-Bonding of the MeHg moiety in these compounds (vs. N-bonding) was established by means of IR, Raman and proton NMR spectroscopy. S-Mercury derivatives provided a means of removing sulfhydryl protective groups from cysteine (147):



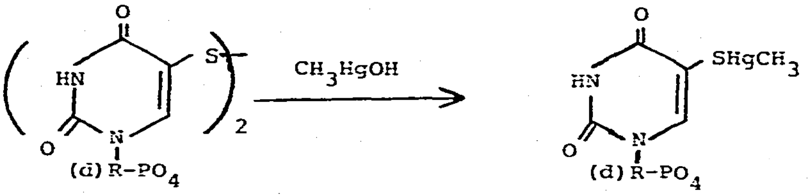
$$\begin{matrix}\text{CH}_2\text{SY}\\ |\\ \text{RNHCHCOR'}\end{matrix} \xrightarrow[\text{or Hg(OAc)}_2\text{ in CF}_3\text{CO}_2\text{H}]{(\text{CF}_3\text{CO}_2)_2\text{Hg in 80\% HOAc}} \begin{matrix}\text{CH}_2\text{SHgO}_2\text{CCF}_3\\ |\\ \text{RNHCHCOR'}\end{matrix} \xrightarrow{\text{H}_2\text{S}} \begin{matrix}\text{SH}\\ |\\ \text{RNHCHCOR'}\end{matrix} + \underline{\text{HgS}}$$

R = H; R' = OH

R = Z-gly; R' = Gly-OMe

Y = Me_3C, p-$MeOC_6H_4$

5-Methylmercurimercapto derivatives of pyrimidine nucleotides have been prepared and tested as substrates for nucleic acid polymerases, among them the 5-MeHgS derivatives of uridine, deoxyuridine and deoxycytidine triphosphates (148). Preparation of 5-methylmercurimercapto-deoxyuridylic acid was recorded:



$CH_2NH_3^+$, and cysteamine, $HSCH_2CH_2NH_3^+$, showed the former to bind methylmercury(II) more strongly (149). The compound $CH_3HgSeCH_2CH_2NH_3^+Cl^-$ was isolated and characterized.
Also reported has been the binding of MeHg(II) by selenohydryl-containing ligands, a study of importance with respect to the problem of chemical protection against mercury toxicity. NMR studies of the binding of selenocysteamine, $HSeCH_2$–

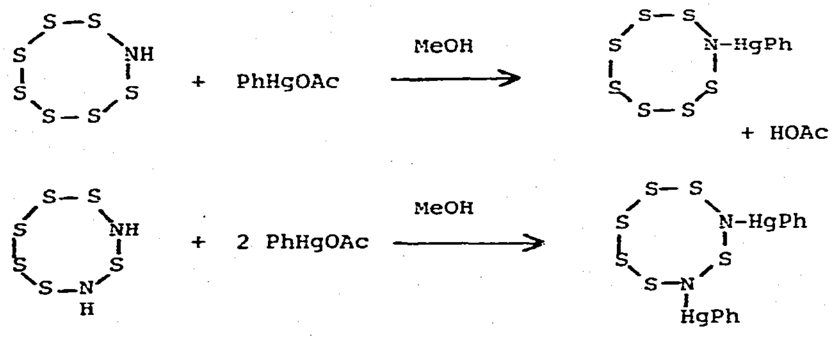
Some Hg-N compounds also have been investigated:
Mercury bis(trifluoromethylmercapto)amino compounds (150):

$$(CF_3Hg)_2O \xrightarrow{(CF_3S)_2NH} CF_3HgN(SCF_3)_2$$

$$HgO \xrightarrow{(CF_3S)_2NH} Hg[N(SCF_3)_2]_2$$

$$(C_6H_5)_2Hg \xrightarrow{(CF_3S)_2NH} C_6H_5HgN(SCF_3)_2 + C_6H_6$$

Mercury derivatives of cycloazaheptathiane and cyclodiazahexathiane (151, 152):



Similar reactions were carried out with 1,4- and 1,5-$(NH)_2S_6$. All of the products were light-sensitive. Methylmercury derivatives were prepared in similar fashion. The thermolysis of cyclo-$PhHgNS_7$ gave HgS, Ph_2Hg, S_8, $(S_7N)_2S_x$, S_4N_2 and S_4N_4. It reacted with covalent halides to give cyclo-NS_7 derivatives (152):

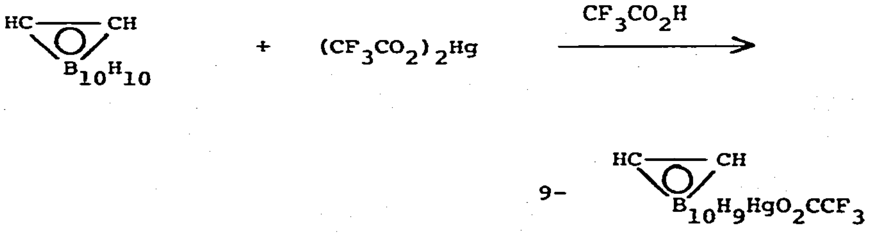
$$\begin{aligned} PhHgNS_7 \;+\; HCl &\xrightarrow{\qquad} HNS_7 \;+\; PhHgCl \\ (COCl)_2 &\xrightarrow{\qquad} (CONS_7)_2 \;+\; PhHgCl \\ Me_3SnCl &\xrightarrow{\qquad} Me_3SnNS_7 \;+\; PhHgCl \end{aligned}$$

Similar reactions with R_3PbCl (R = Me, Et), $SOBr_2$, SCl_2 and S_2Cl_2 gave R_3PbNS_7, $OS(NS_7)_2$, $S_{15}N_2$ and $S_{16}N_2$, respectively. Reaction with Ph_2PCl resulted in the unexpected formation of $Ph_2P(S)NS_7$, and the action of Ph_2PCl on 1,4-$(PhHgN)_2S_6$ gave 1,4-$(Ph_2P(S)N)_2S_6$.

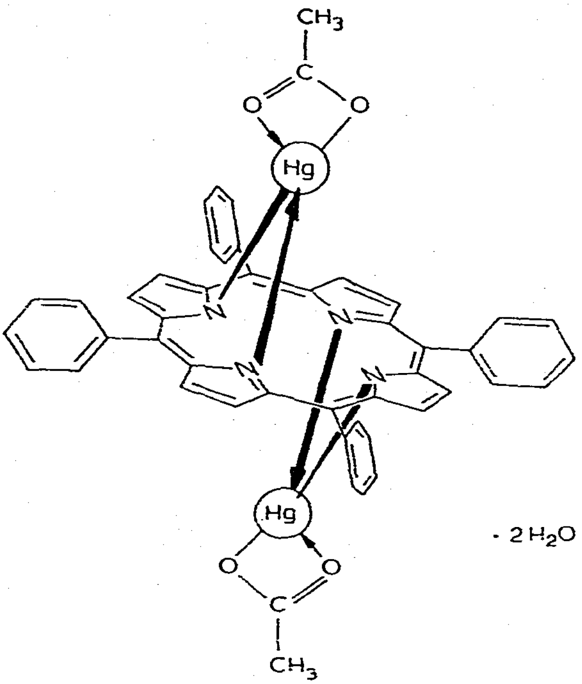
Although they are not organomercury compounds in the strict sense, we note the preparation and characterization of the interesting complex µ-*meso*-tetraphenylporphyrinato-bis(mercury(II) acetate, **34**, as well as of N-methyloctaethylporphyrinatomercury(II) acetate, **35**, by Hudson and Smith in a continuation of their studies in this area (152a).

B. Mercurials with Metalloidal and Metal Substituents

Bregadze et al. have reported the B-mercuration of *o*- and *m*-carborane (153):



$$m\text{-}HC(B_{10}H_{10})CH \;+\; (CF_3CO_2)_2Hg \xrightarrow{CF_3CO_2H} m\text{-}HC(B_{10}H_9HgO_2CCF_3\text{-}9)CH$$



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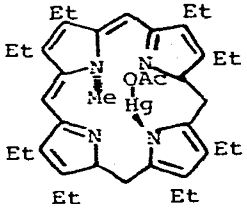


35

Brominolysis served to establish the structures of these products.

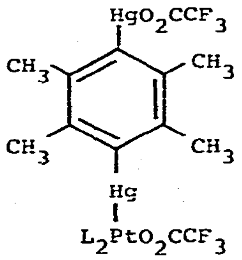
Stable compounds containing the Hg-Pt linkage have been prepared by Reutov and his coworkers (39, 154); some of this work has been discussed in Section 3A. Further results include:

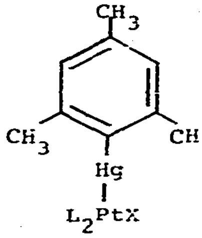
$$R_fHgX \quad + \quad (Ph_3P)_3Pt \longrightarrow R_fHgPt(PPh_3)_2X$$

(X = R_f or halogen)

Prepared in this manner were:

$C_6F_5HgPtL_2C_6F_5$ (L = PPh_3)





($X = Cl, O_2CCF_3$)

It would appear that steric factors, as well as electronic factors, are important in contributing to the stability of such complexes. Treatment of these compounds with trifluoroacetic acid resulted in liberation of elemental mercury:

$$C_6F_5HgPtL_2C_6F_5 + CF_3CO_2H \longrightarrow C_6F_5PtL_2O_2CCF_3 + Hg + C_6F_5H$$

Oxymercuration products of olefins underwent deoxymercuration on treatment with low-valent platinum complexes:

$$Ph_2C(OMe)CH_2HgBr + L_2Pt(dba) \longrightarrow Ph_2C{=}CH_2 +$$

(dba = dibenzylidene acetone)

$L_2Pt(HgBr)OMe$

or

$L_2Pt(HgOMe)Br$

C. Mercurials with Group IV Substituents

Structural studies on $(Me_3Si)_2Hg$ (X-ray diffraction, IR and Raman spectroscopy) have established the expected linear arrangement in solid state, Si-Hg-Si, with an Si-Hg bond length of 2.500 ± 0.005 Å, and in hexane solution (155).

Bis(phenyldimethylsilyl)mercury has been prepared by the hydride procedure (156):

$$2\ PhMe_2SiH + (Me_3C)_2Hg \xrightarrow{105°,\ 14h} (PhMe_2Si)_2Hg + 2\ i\text{-}C_4H_{10}$$

The pale yellow-green product, like the other Group IV element-mercury compounds, reacts with the oxygen in the air ($\longrightarrow PhMe_2SiOSiMe_2Ph + Hg$) and is subject to photolytic decomposition to give $PhMe_2SiSiMe_2Ph$ and elemental mercury. Photolysis in the presence of triethylgermane was studied:

$$\begin{tikzcd}(PhMe_2Si)_2Hg + 2\ Et_3GeH \arrow[r, "h\nu"] & 2\ PhMe_2SiH + (Et_3Ge)_2Hg \arrow[d, "h\nu"] \\ & Et_3GeGeEt_3 + Hg\end{tikzcd}$$

Reactions with acetic acid, benzoyl peroxide, 1,2-dibromoethane and mercuric chloride all resulted in formation of elemental mercury:

$$(PhMe_2Si)_2Hg \quad + \quad HOAc \longrightarrow PhMe_2SiH + PhMe_2SiOAc + Hg$$

$$+ \quad Bz_2O_2 \longrightarrow 2\ PhMe_2SiO_2CPh + Hg$$

$$+ \quad BrCH_2CH_2Br \longrightarrow 2\ PhMe_2SiBr + C_2H_4 + Hg$$

$$+ \quad HgCl_2 \longrightarrow 2\ PhMe_2SiCl + 2\ Hg$$

Bis[tris(trimethylsilylmethyl)stannyl (and germyl)]mercury have been prepared by way of the thallium derivative (157) and tris(pentafluorophenyl)germylmercurials <u>via</u> an appropriate digermane (158):

$$[(Me_3SiCH_2)_3M]_3Tl + Hg \longrightarrow [(Me_3SiCH_2)_3M]_2Hg$$

(M = Ge, Sn)

$$(C_6F_5)_3GeGeEt_3 + EtHgCl \xrightarrow{\text{THF, }20^\circ} (C_6F_5)_3GeHgEt + Et_3GeCl$$

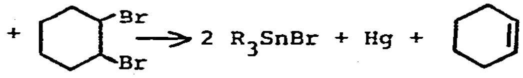
$$2\ (C_6F_5)_3GeGeEt_3 + HgCl_2 \xrightarrow{\text{THF, }20^\circ} [(C_6F_5)_3Ge]_2Hg + 2\ Et_3GeCl$$

The chemical conversions of bis(trineopentylstannyl)mercury have been examined in some detail (159):

$$[(Me_3CCH_2)_3Sn]_2Hg \xrightarrow{h\nu, 50°} R_3SnSnR_3 + Hg \quad (R = Me_3CCH_2)$$

$$\xrightarrow{180-200°} R_3SnSnR_3 + Hg$$

$$+ S_8 \longrightarrow (R_3Sn)_2S + Hg$$



$$+ (R_f)_2Hg \longrightarrow 2\ R_3SnF + Hg + \text{perfluoro-olefin}$$

On mixing in 1:1 ratio with bis(triethylgermyl)mercury, redistribution occurs to only a small extent:

$$(R_3Sn)_2Hg + (Et_3Ge)_2Hg \rightleftharpoons 2\ R_3SnHgGeEt_3$$

Photolysis gave R_3SnSnR_3, $Et_3GeGeEt_3$ and $R_3SnGeEt_3$, the latter in only 13% yield. Some mixed alkyl(triethylgermyl)mercury compounds have been prepared (159):

$$Et_3GeHgGeEt_3 + RX \xrightarrow{h\nu} Et_3GeX + RHgGeEt_3$$

$$(RX = Me_3SiCH_2Cl,\ Me_3CCH_2Br)$$

$$Et_3GeHgGeEt_3 + RHgCl \longrightarrow RHgGeEt_3 + Et_3GeCl$$

The reactions of $(R_3Si)_2Hg$, $(R_3Ge)_2Hg$ and $(R_3Sn)_2Hg$ compounds with mercurated diazoacetic esters are of particular interest (160, 161):

$$\begin{tikzcd} (MePh_2Si)_2Hg + Hg[C(N_2)CO_2Et]_2 \arrow[r, "60-70°"] & {[2\ MePh_2SiHgC(N_2)CO_2Et]} \arrow[d] \\ & 2\ Hg + 2\ MePh_2SiC(N_2)CO_2Et \end{tikzcd}$$

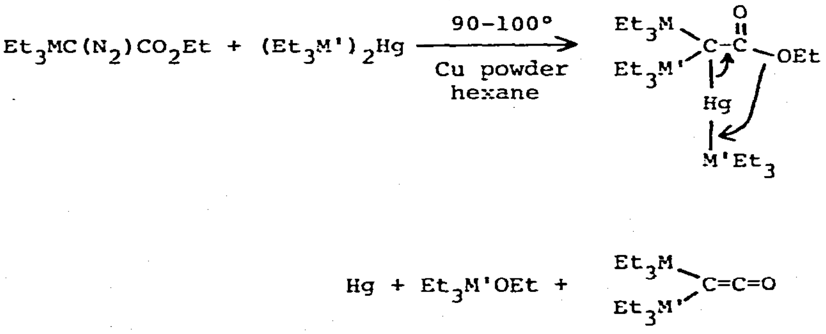
$$(Et_3Ge)_2Hg + Hg[C(N_2)CO_2R]_2 \longrightarrow 2\ Et_3GeC(N_2)CO_2R + 2\ Hg$$

(R = Me, Et)

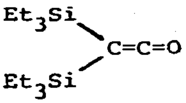
$$(R'_3Sn)_2Hg + Hg[C(N_2)CO_2R]_2 \longrightarrow 2\ R'_3SnC(N_2)CO_2R + 2\ Hg$$

$(R' = Me_3CCH_2)$

Reactions of the product diazoacetic ester derivatives with Group IV mercurials gave novel dimetalated ketenes:



Such reactions of $Et_3SiC(N_2)CO_2Et$ with $(Et_3Si)_2Hg$ and $(Et_3Ge)_2Hg$, of $Et_3GeC(N_2)CO_2Et$ with $(Et_3Ge)_2Hg$ and of $Et_3SnC(N_2)CO_2Et$ with $(Et_3Ge)_2Hg$ were carried out, giving the ketenes 36, 37, 38 and 39.



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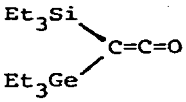

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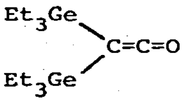

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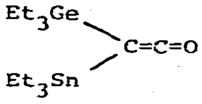

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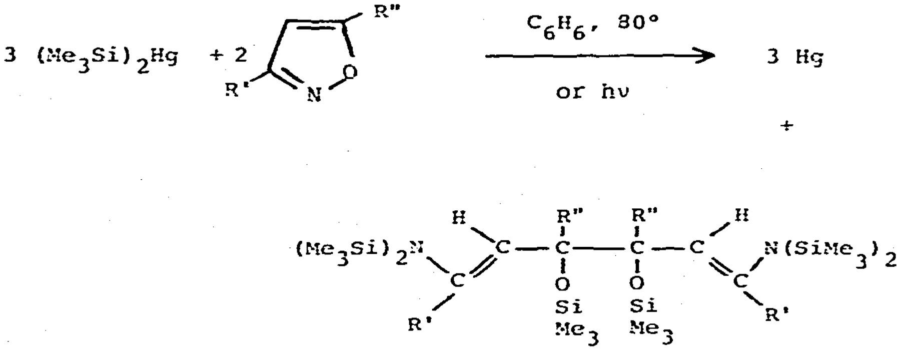
The reaction of bis(trimethylsilyl)mercury with isoxazole and methyl-substituted isoxazoles resulted in formation of 1,5-hexadiene derivatives (162):



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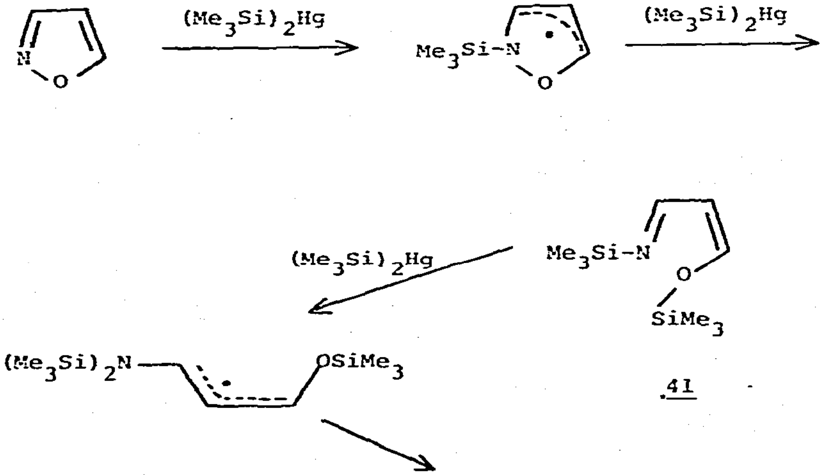
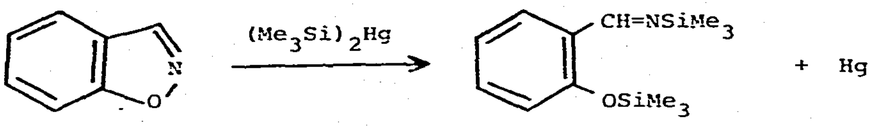


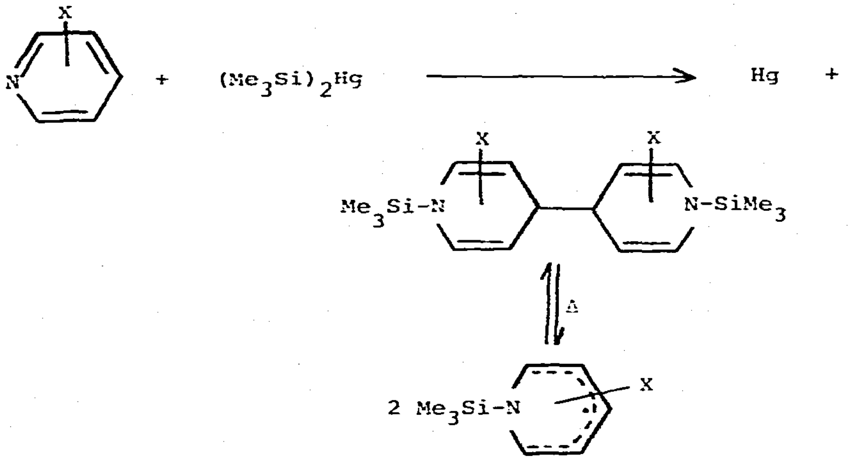
40 (R' = R" = H)

Compounds of type 41 are obtained as the end-products in the case of benz[d]isoxazole:



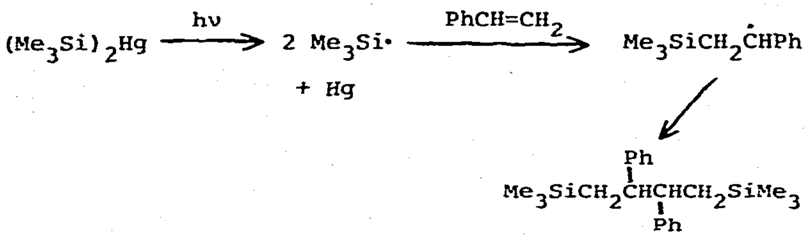
Curiously, the isoxazole system does not undergo such reactions with $(Me_3C)_2Hg$ and $(Me_3Ge)_2Hg$.

Bis(trimethylsilyl)mercury reacts with 3- and 4-trialkyl-(Group IV)metal compounds of pyridine to form N,N'-bis(trimethylsilyl)tetrahydro-4,4'-bipyridyls (163):



In the examples cited, X = H, 2-Me, 3-Me, 4-Me, 3-CN, 4-CN, 3-CO_2Me, 4-CO_2Me, 4-COMe. Thermal dissociation of the products gave the respective stable pyridyl free radicals. Bis(trimethylgermyl)mercury did not react analogously except when electron-withdrawing substituents such as CN, CO_2Me and $CONEt_2$ were present in the pyridine ring.

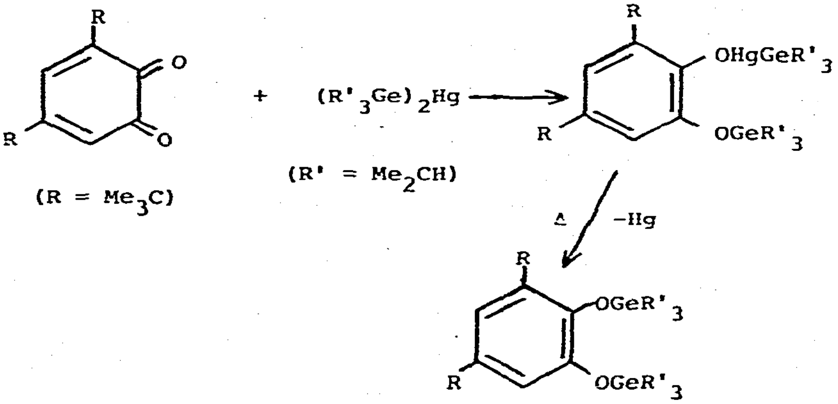
In view of the known homolytic fission of bis(trimethylsilyl)mercury on irradiation with ultraviolet light to give trimethylsilyl radicals, it is not surprising that this compound can be used to initiate the photopolymerization of styrene (164). Trimethylsilyl groups were found to be incorporated into the polymer. A 1:1 photo-induced reaction of $(Me_3Si)_2Hg$ with styrene gave <u>42</u>:

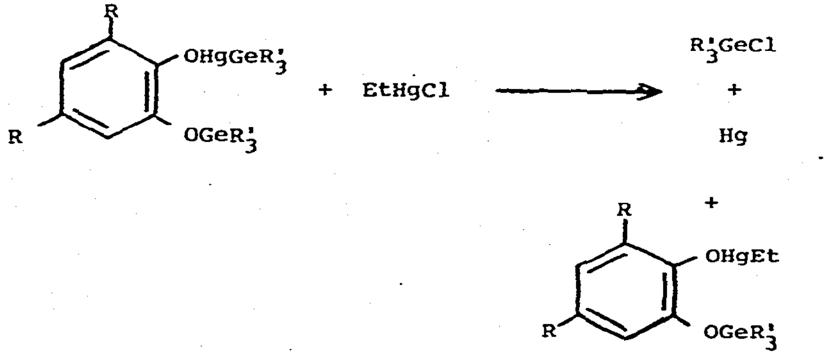


42

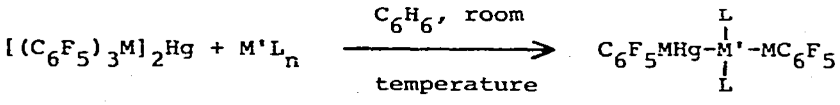
In other experiments, the trimethylsilyl radical was captured by spin-trapping with 2,4,6-tri-tert-butylnitrosobenzene.

The first stable compound containing the O-Hg-Ge system has been prepared by way of bis(triisopropylgermyl)mercury (165):





Group IV-mercury compounds also have served in the synthesis of novel transition metal complexes <u>via</u> L_2Pt and L_2Pd ($L = Ph_3P$) insertion into the Hg-Group IV element bond (166):



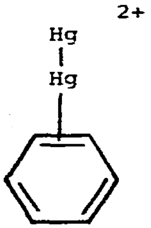
$$[(C_6F_5)_3M]_2Hg + M'L_n \xrightarrow[\text{temperature}]{C_6H_6,\ \text{room}} C_6F_5MHg-\overset{L}{\underset{L}{M'}}-MC_6F_5$$

43, $M = Ge$, $M' = Pt$
44, $M = Ge$, $M' = Pd$
45, $M = Sn$, $M' = Pt$

Finally, the reaction of hexamethyldilead with methylmercuric chloride very likely proceeds by way of a transient $Me_3PbHgMe$ intermediate to give tetramethyllead, dimethylmercury, lead(II) chloride and elemental mercury (167). A similar reaction with CD_3HgCl gave CH_3HgCD_3.

8. COMPLEXES OF ORGANOMERCURIALS

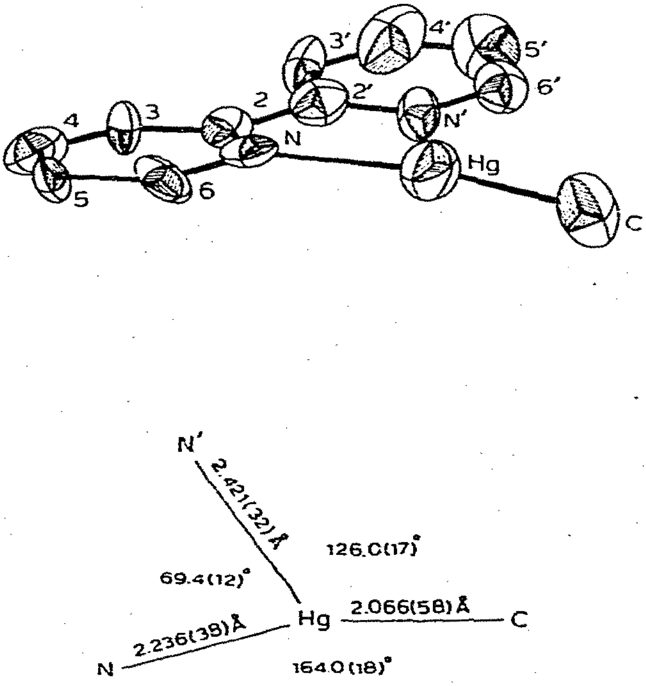
Arene complexes of mercury(I) hexafluoroarsenate have been studied by Dean, Ibbott and Stothers in liquid sulfur dioxide using Raman and ^{13}C NMR spectroscopy (168). 1:1 Complexes were obtained between $Hg_2(AsF_6)_2$ and benzene, biphenyl, naphthalene, 2-methyl- and 2,6-dimethylnaphthalene, acenaphthene, fluoranthene, fluorene, phenanthrene, anthracene, 9,10-dimethylanthracene and m-dinitrobenzene. On the basis of the spectroscopic results, it was suggested that localized bonding, as in 46, was operative in these complexes.



46

Australian workers have investigated organomercury compounds containing three-coordinate mercury of type $[MeHgL]NO_3$, where L = pyridine and all three methylpyridine isomers, 2-benzylpyridine, 2,4- and 2,6-dimethylpyridine, 2,2'-bipyridine and various isomeric dimethylbipyridines, 9, 10-phenanthroline and three of its dimethyl derivatives. According to spectroscopic studies (IR, proton NMR), the substituted bipyridine and phenanthroline complexes in solution contain three-coordinate mercury (169). The crystal structure of [MeHgbipy]NO_3 confirmed that this also is the case in the solid state, and Fig. 3 shows the planar cation which is present (170). The thermochemistry of adduct formation between arylmercuric halides and 4-methylpyridine, 1,10-phenanthroline and N,N,N',N'-tetramethylethylenediamine has been studied by Graddon and Mondal (171). As expected, the bidentate ligands form much stronger complexes than 4-methylpyridine. In both cases, however, the enthalpies of formation were low since rather weak Hg-N bonds are involved. Data of interest are summarized in Table 17 and 18. Evidence obtained indicated that tertiary phosphines cause symmetrization of arylmercuric halides:

Figure 3. Structure of the planar cation in $[CH_3Hg(bipy)]^+$ NO_3^-, and the stereochemistry of mercury. From A. J. Canty and A. Marker, Inorg. Chem., 15 (1976) 426.



$$2\ ArHgX + 2\ PR_3 \longrightarrow Ar_2Hg + HgX_2(PR_3)_2$$

The complexes of mercuric cyanide with N-donor molecules have been investigated by several groups:

- $Hg(CN)_2$ Complexes with 2,2'-bipyridine, 1,10-phenanthroline and 2,9-dimethyl-1, 10-phenanthroline (IR study) (172).
- $Hg(CN)_2$ Complexes with 1,10-phenanthroline, 2,2'-bipyridine and ammonia (solid adducts), with ethylamine, 1,3-diaminopropane, diethylenetriamine and diethylenetetramine (stability constants determined pH-metrically in aqueous solution at 25°) (173).
- $Hg(CN)_2$ Complexes with 4,4'-bipyridine (polymeric chain structure) and 4,4'-(propane-1,3-diyl)bispyridine (174).

9. STRUCTURAL STUDIES

X-ray diffraction has been used to determine the structures of a number of organomercurials and inorganic mercury compounds which will be of interest to the organometallic chemist. A few of these have been discussed in previous sections. The others include the following:

Phenylmercuric cyanide was found to have a structure consisting of discrete molecular units with an approximately linear C-Hg-C-N group (Fig. 4) (175).

In methyl(N,N-diethyldithiocarbamato)mercury the mercury atom is two-coordinate with a C-Hg-S bond angle of 171.2° (176). However, two molecules around the center of symmetry are loosely bridged by two sulfur atoms. The resulting structure with its HgS_2Hg bridging unit is shown in Fig. 5 .

The novel σ-cyclopentadienylmercury derivative $(Ph_3PC_5H_4HgI)_2$ has been prepared by the reaction of triphenylphosphonium cyclopentadienylide and mercuric iodide. Its structure is shown in Fig. 6 (177). ^{13}C and ^1H NMR studies of this compound in solution suggested that fluxional σ-bonding is involved.

Russian workers have determined the structures of mercurials of type <u>47</u> (Fig. 7 a, b and c) (178, 179). It is apparent from the Hg-<u>ortho</u>-halogen distances that there is no significant intramolecular or intermolecular Hg...X interaction. Instead, an intermolecular Hg...O interaction, d(Hg-O) = 2.78Å, appears to be present.

Other molecules whose structures have been reported include $C_5H_5NHgOAc^+OAc^-$ (Fig. 8) (180), which may be considered as a model of the active electrophilic species in

(Continued on p. 274)

TABLE 17. Thermodynamic Data for Formation of 1:1 Adducts of ArHgX with 4-Methyl-Pyridine in Benzene Solution at 30°C (CONC. of ArHgX in mmol l^{-1}, K in $l\ mol^{-1}$, ΔH^0, ΔG^0 in $kJ\ mol^{-1}$, ΔS^0 in $J\ K^{-1}\ mol^{-1}$). From D. P. Graddon and J. Mondal, J. Organometal. Chem., 107 (1976) 1.

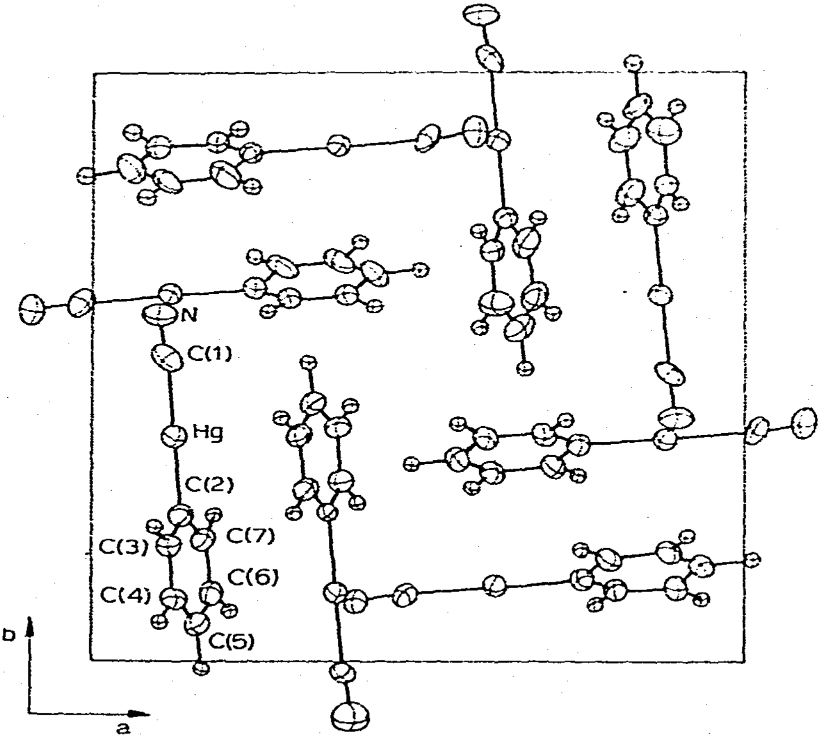
Ar	X	[ArHgX]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
C_6H_5	Br	2.0	1.8±0.3	30.0[a]	1.5±0.5	
o-$CH_3C_6H_4$	Cl	13.0-17.0	1.4±0.2	21.5±2.8	0.9±0.5	68±11
p-$CH_3C_6H_4$	Cl	7.0-9.0	2.8±0.4	20.7±1.5	2.6±0.4	60±7
o-$CH_3OC_6H_4$	Cl	15.0-30.0	2.4±0.2	24.2±1.5	2.2±0.3	72±6
p-$C_2H_5OC_6H_4$	Cl	10.0-14.0	1.6±0.2	27.5±1.1	1.2±0.4	87±5
p-ClC_6H_4	Cl	7.0-14.0	2.6±0.3	28.6±0.9	2.4±0.4	86±5
o-ClC_6H_4	Cl	15.0-25.0	2.3±0.2	30.1±1.1	2.1±0.3	92±5
C_6Cl_5	Cl	1.8-2.0	3.4±0.7	37.6±3.7	3.1±0.6	114±15

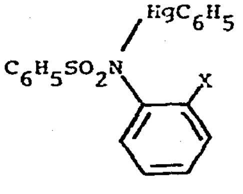
[a] Arbitrary value.

TABLE 18. Thermodynamic Data for Formation of 1:1 Adducts of ArHgX with phen and tmed in Benzene Solution at 30°C (CONC. of ArHgX in mmol l^{-1}, K in $l\ mol^{-1}$, ΔH^0, ΔG^0 in $kJ\ mol^{-1}$, ΔS^0 in $J\ K^{-1}\ mol^{-1}$). From D. P. Graddon and J. Mondal, J. Organometal. Chem., 107 (1976) 1.

Ar	X	Base	[ArHgX]	K	$-\Delta H^0$	$-\Delta G^0$	$-\Delta S^0$
C_6H_5	Br	phen	1.0-2.0	798±113	20.2±0.3	16.9±0.4	11±2
C_6H_5	Br	tmed	1.5-2.0	211±71	26.3±1.6	13.5±1.0	42±8
C_6H_5	Cl	phen	1.5-2.0	346±13	30.6±0.5	14.7±0.1	49±2
C_6H_5	Cl	tmed	1.7-2.0	137±11	33.2±0.5	12.4±0.3	69±3
o-$CH_3C_6H_4$	Cl	phen	1.0-4.0	221±27	29.2±1.3	13.6±0.3	51±5
p-$CH_3C_6H_4$	Cl	phen	3.0-5.0	298±13	23.7±0.6	14.4±0.2	31±8
p-$CH_3C_6H_4$	Cl	tmed	1.5-3.0	71±4	37.0±1.3	11.7±0.2	83±5
o-$CH_3OC_6H_4$	Cl	phen	2.5-3.5	193±33	23.2±2.0	13.3±0.4	33±8
p-$C_2H_5OC_6H_4$	Cl	phen	2.3-2.8	233±6	26.1±0.6	13.7±0.1	41±2
o-ClC_6H_4	Cl	phen	3.0-4.0	967±134	29.6±1.0	17.3±0.4	41±5
p-ClC_6H_4	Cl	phen	3.0-4.0	719±65	26.7±0.4	16.6±0.3	33±3
p-ClC_6H_4	Cl	tmed	1.5-2.5	170±16	39.9±1.2	12.9±0.3	89±5
p-ClC_6H_4	Br	tmed	2.0-2.5	228±25	31.5±1.6	13.7±0.3	59±6
C_6Cl_5	Cl	phen	1.5-2.0	>8000	28.4±1.7	>22	<21
C_6Cl_5	Cl	tmed	1.8-2.0	670±43	44.8±1.5	16.4 0.2	94±6

Figure 4. Structure of phenylmercuric cyanide (projection of the structure along *c*, showing the thermal ellipsoids at 40% probability. From G. Gill, F. H. Cano and S. Garcia-Blanco, Acta Cryst., B32 (1976) 2680.





47

(X = F, Cl, Br)

olefin mercuration by mercuric acetate in THF, bis(acridine)-dimercury(I) perchlorate (Fig. 9) (181) and mercury(II) tropolonate which involves Hg-O (not Hg-C) bonding (Fig. 10) (182).

(Continued on p. 279)

Figure 5. Structure of methyl(N,N-diethyldithiocarbamato)-mercury (ORTEP plot of the molecule showing the HgS_2Hg grouping. From C. Chieh and L. P. C. Leung, Can. J. Chem., 54 (1976) 3077.

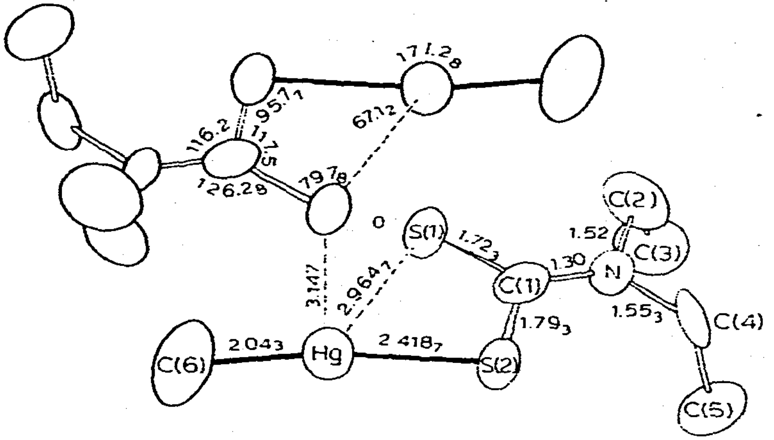


Figure 6. Structure of $(Ph_3PC_5H_4HgI)_2$ (ORTEP plot). From N. L. Holy, N. C. Baenziger, R. M. Flynn and D. C. Swenson, J. Amer. Chem. Soc., 98 (1976) 7823.

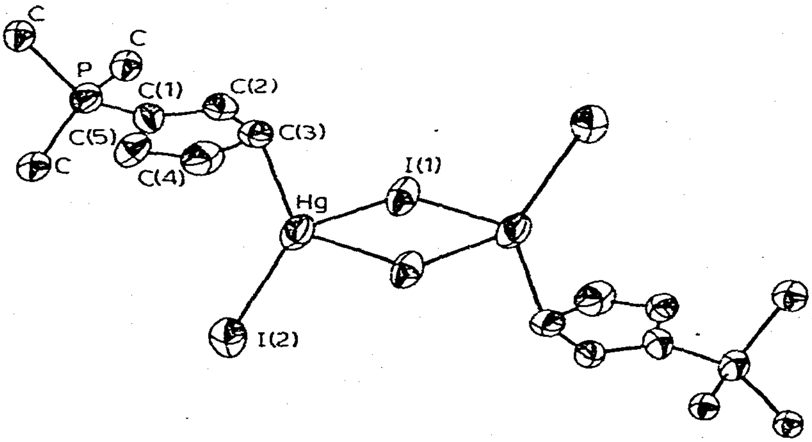
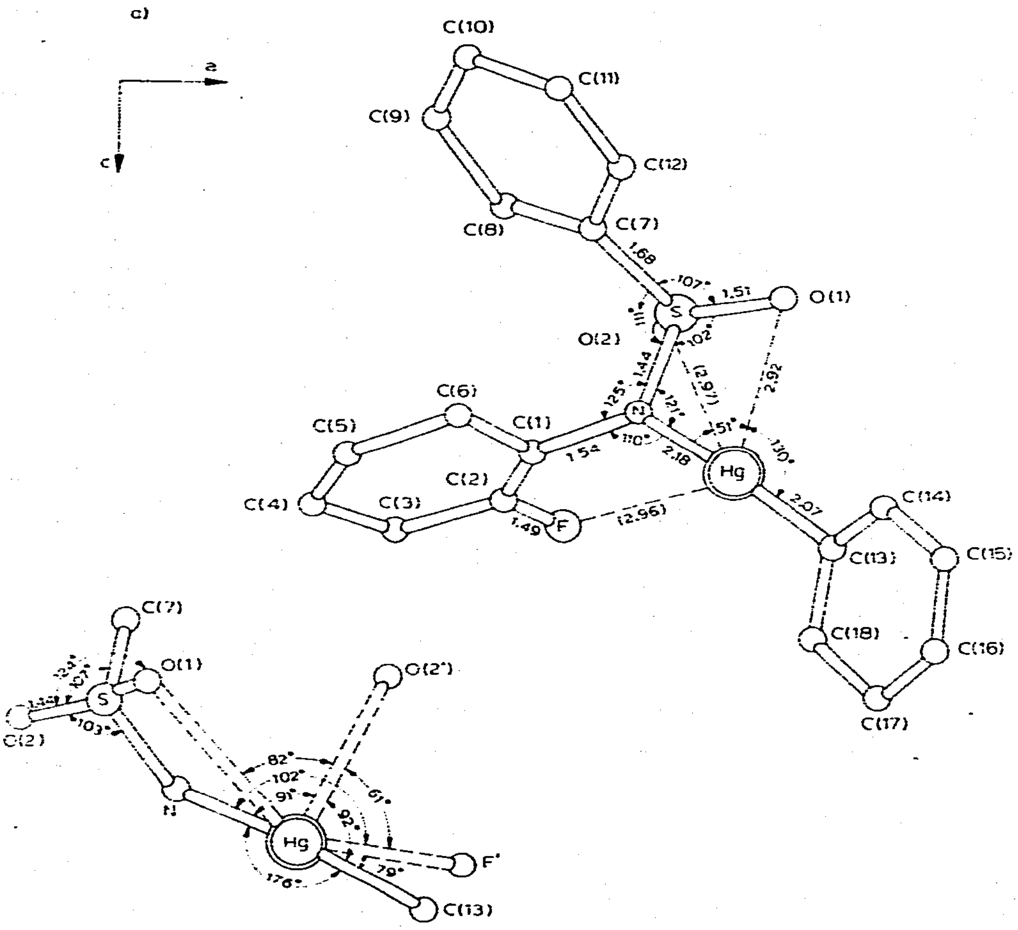
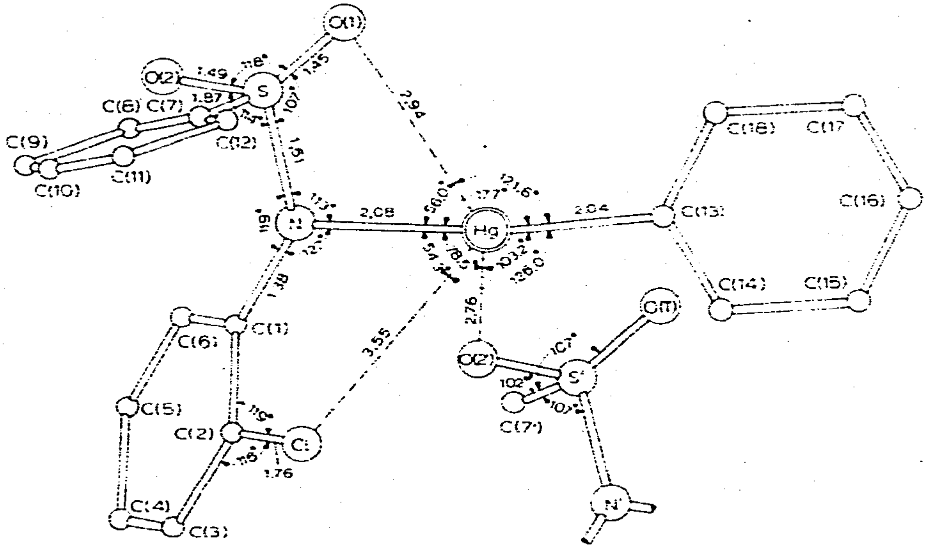


Figure 7. Structures of $C_6H_5SO_2N(HgC_6H_5)C_6H_4X$-o (X = F (fig. 7a), Cl (fig. 7b) and Br (fig. 7c). From L. G. Kuzmina, N. G. Bokii, Yu. T. Struchkov, D. N. Kravtsov and A. S. Peregudov, Zh. Strukt. Khim., 17 (1976) 333 and 342.



b)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C(11)
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119°
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Hg
2.04
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121.6°
103.2°
126.0°
1.38
C(1)
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C(5)
C(2)
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116°
Cl
1.76
C(4)
C(3)
O(2')
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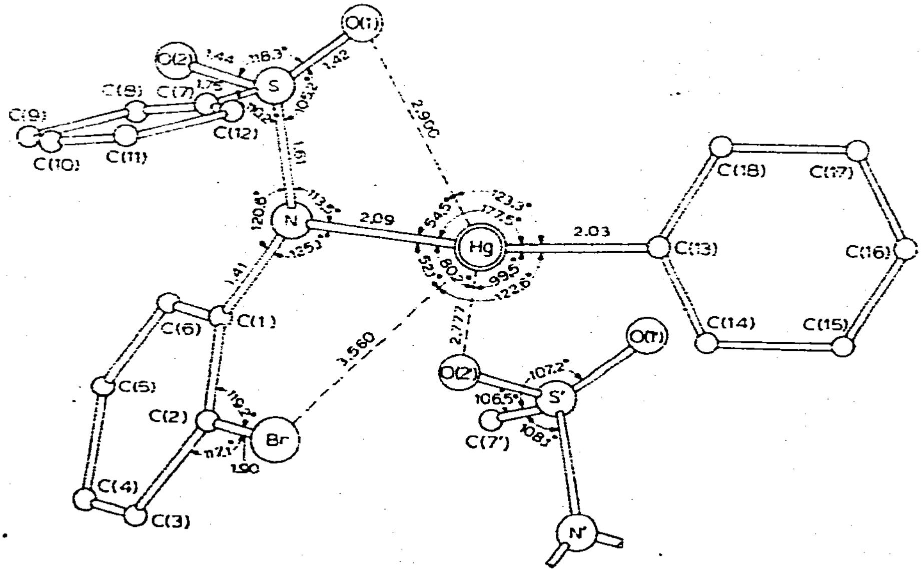

O(1)
O(2)
1.44
118.3°
1.42
S
C(8)
C(7)
1.75
C(9)
C(10)
C(11)
C(12)
2.900
1.61
120.8°
N
113.5°
2.09
125.1°
Hg
54.5°
177.5°
123.3°
2.03
C(13)
52°
80.2°
99.5°
122.6°
1.41
C(1)
C(6)
3.560
2.777
C(5)
C(2)
119.2°
Br
117.1°
1.90
C(4)
C(3)
O(2')
S'
O(1')
107.2°
106.5°
108.1°
C(7')
N'
C(18)
C(17)
C(16)
C(14)
C(15)

Figure 8. Structure of $C_5H_5NHgOAc^+$ OAc^-. From D. Grdenic, B. Kamenar and A. Hergold-Brundic, Cryst. Struct. Comm., 5 (1976) 769.

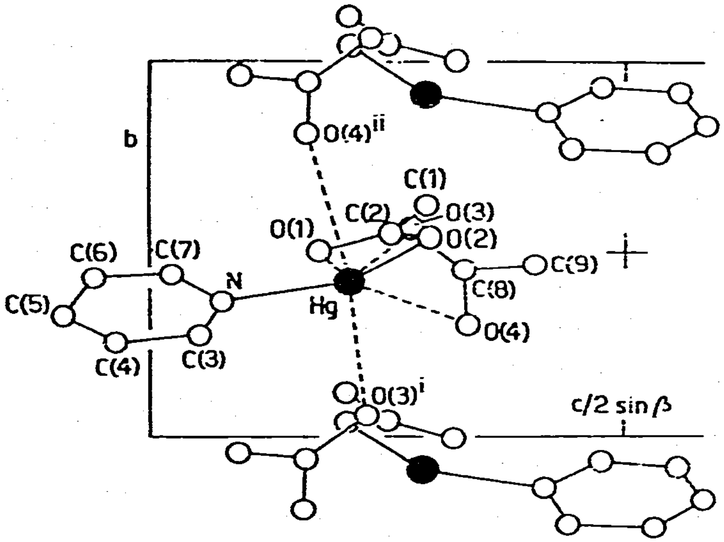


Figure 9. The structure of $[Hg_2(acridine)_2](ClO_4)_2$ (the thermal ellipsoids are drawn at 50% probability, with H atoms assigned a radius of 0.15Å. From D. Taylor, Austral, J. Chem., 29 (1976) 723.

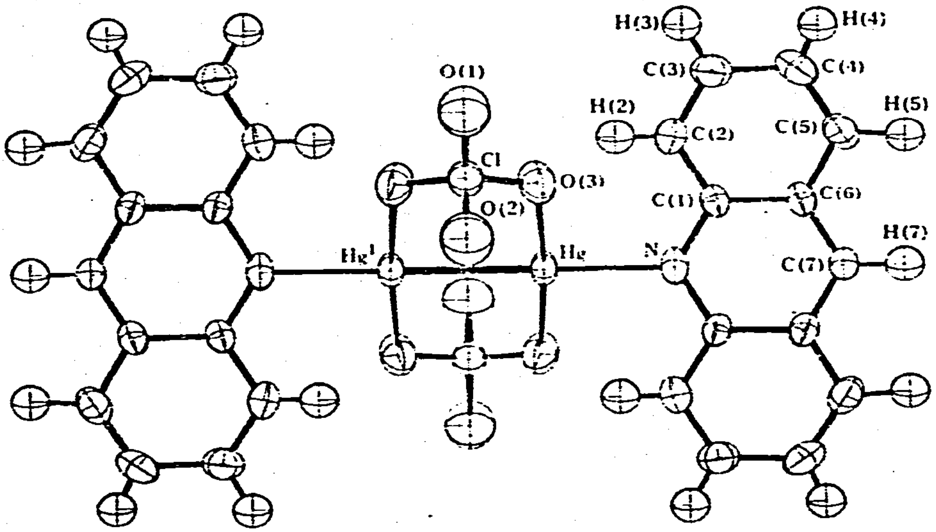
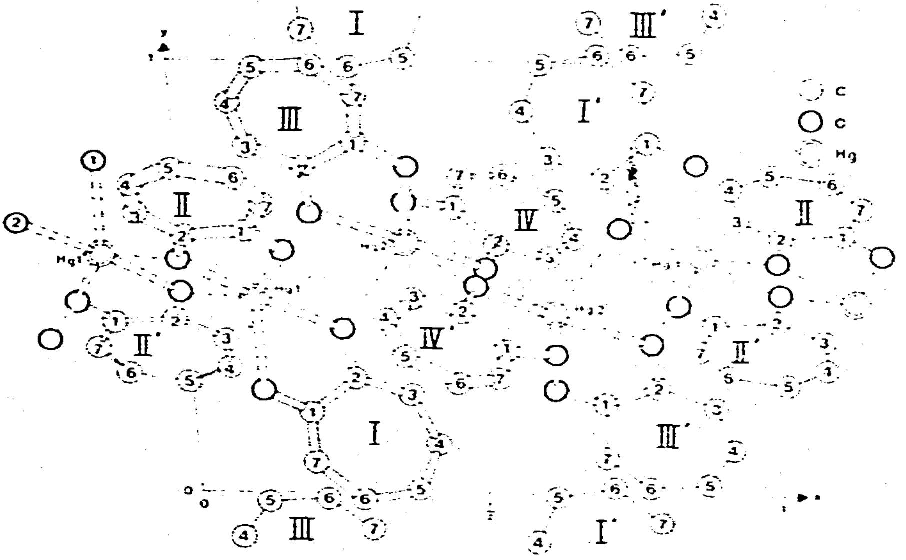


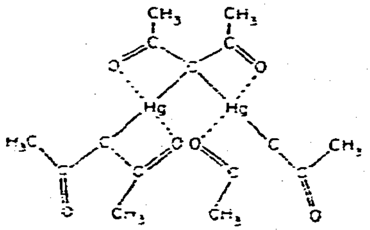
Figure 10. Structure of mercury(II) tropolonate (projection onto the x,y plane). From R. Allmann, K. Dietrich and H. Musso, Justus Liebigs Ann. Chem. (1976) 1185.



10. SPECTROSCOPIC STUDIES

A. Vibrational Spectroscopy

The IR and Raman spectra of CH_3HgX and CD_3HgX (X = Cl, Br, I) in solution and in the solid state have been measured and complete assignment of the fundamentals was made (183), and force constant calculations on CH_3HgY (Y = Me, F, Cl, Br, I, CN, SCN, $AsMe_2$, SMe, SHgMe and $S^+(HgMe)_2$) have been carried out (184). The vibrational spectra of $MeHgS_2CNEt_2$ (176) and of 1:1, 1:2 and 2:3 Hg(II)-acetylacetone complexes (185) have been reported. In the latter, it was established that the mercury is bound to the γ-carbon atom of the acac ligand in each complex. One or both of the hydrogens of the γ-carbon atom may be replaced by mercury. Suggested structures for the three types of complexes are shown below as formulas <u>48</u>, <u>49</u> and <u>50</u>. The IR and Raman spectra of various $Hg(SR)_2$ compounds (R = Me, Et, t-Bu) showed that the first two have linear, two-coordinate Hg, while the t-BuS compound contains tetrahedral, four-coordinate mercury (186). This study allowed



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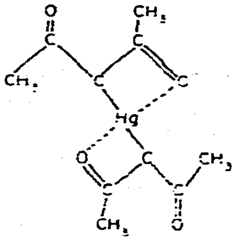

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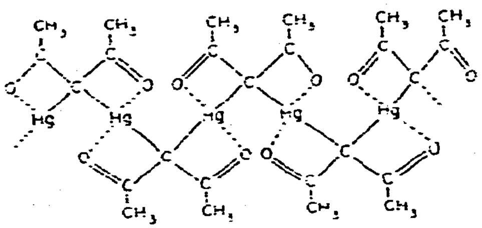

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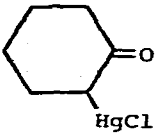
the authors to assign a polymeric structure with linear coordination to the 1:1 Hg(II)/$HOCH_2CH(SH)CH_2SH$ (British Anti-Lewisite) complex. The IR spectrum of CF_3SHgCl has been studied (187).

Raman spectroscopy and polarography have been used to investigate the effect of σ-π conjugation in α-mercurated aldehydes and ketones [$HC(O)CH_2HgCl$, $(HC(O)CH_2)_2Hg$, $EtC(O)CH_2HgCl$, $(EtC(O)CH_2)_2Hg$, 51 and 52] (188). It was



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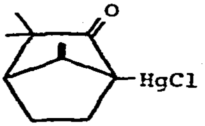


52

concluded that σ-π-conjugation is of importance in all of these compounds except 52.

(Continued on p. 284)

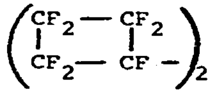
TABLE 19. Solvent Dependence of $J(^{199}Hg\text{-}C\text{-}^{19}F)$ and $J(^{199}Hg\text{-}C\text{-}C\text{-}^{19}F)$ in Symmetrical Polyfluoroalkylmercurials. From L. A. Fedorov, Z. A. Stumbrevichyute and E. I. Fedin, Zh. Strukt. Khim., 16 (1975) 976.

R_2Hg	Solvent	${}^2J_{^{199}Hg\text{-}C\text{-}^{19}F}$, Hz	${}^3J_{^{199}Hg\text{-}C\text{-}C\text{-}^{19}F}$, Hz
1	2	3	4
$(CF_3)_2Hg$	CCl_4	1245,3	
	C_6H_6	1260,0	
	CH_2Cl_2	1263,5	
	CH_3NO_2	1297,1	
	CH_3CN	1299,6	
	DME	1313,8	
	Pyridine	1325,1	
	DMSO	1325,2	
	DMF	1326,1	
$(CF_3CF_2)_2Hg$	CCl_4	793	61,4
	CH_2Cl_2	787	60,8
	C_6H_6	755	70,2
	THF	749,5	76,4
	DME	745	78,1
	$HOCH_2CH_2OH$	738	81,1
	Pyridine	684	88,6
	$p\text{-}BuNH_2$	643,5	92,2
	Piperidine	629,5	92,3
	$NH_2CH_2CH_2NH_2$	623,5	92,1
$[(CF_3)_3C]_2Hg$	C_6H_{12}		142,8
	CCl_4		143,0
	CH_2Cl_2		142,4

TABLE 19. (cont'd)

	C_6H_6		144,2
	DME		142,7
	Pyridine		127,2
	DMSO		147,9
	Acetone		150,9
	DMF		154,5
$[(CF_3)_2CH]_2Hg$	C_6H_{12}		174,0
	CCl_4		174,5
	CH_2Cl_2		178,2
	C_6H_6		181,0
	$(C_2H_5)_2O$		186,4
	Dioxane		190,5
	THF		196,4
	CH_3CN		196,9
	DME		199,2
	Pyridine		206,0
$(CF_3CFCl)_2Hg$	CCl_4	689	80,7
	CH_2Cl_2	680	81,4
	C_6H_6	648	87,8;88,7
	DME	585	102,8;104,0
	Pyridine	533	112,1;112,5
$[(CF_3)_2CF]_2Hg$		545,8	113,9
	C_6H_{12}	514	114,4
	CCl_4	535	115,2
	CH_2Cl_2	507	116,4
	C_6H_6	490	119,6
	CH_3NO_2	488	122,6
	Dioxane	466	125,4
	Pyridine	338	132,5
	DME	387	135,6

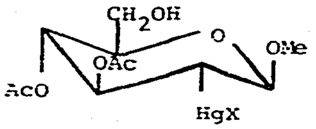
TABLE 19. (cont'd)

	DMF	405	137,4
	DMSO	387	139,4
$[(CF_3)_2CC(O)F]_2Hg$	C_6H_{12}		162,2
	CCl_4		163,4
	C_6H_6		163,7
	DME		164,0
	DMF		208,1
$(CF_3CH_2)_2Hg$	CCl_4		219,5
	CH_2Cl_2		229,2
	DME		251,4
	Pyridine		261,5
$(CF_3CFH)_2Hg$	CCl_4	511	144,7 and 145,8
	CH_2Cl_2	510	149,9
	C_6H_6	490	153,7 and 158,0
	Acetone	491	169,7 and 168,9
	DME	496 and 494	172,4 and 175,1
	Pyridine	443 and 450	188,7 and 190,8
$(CFHCOOC_2H_5)_2Hg$	CH_2Cl_2	538,7	
	C_6H_6	530 and 537	
	DME	535 and 533	
	Pyridine	497	
	DMF	541 and 544	
	CH_2Cl_2	568	144,2
$(CF_3CFCOOC_2H_5)_2Hg$	DME	491	167,4 and 178,0
 Hg	C_6H_6	500	
	DME	415	

B. NMR Spectroscopy

Kennedy and McFarlane have obtained ^{199}Hg shielding anisotropies in dimethylmercury and the methylmercuric halides from studies of the molecules of these compounds which were partially oriented in nematic phases of a liquid crystal solvent (189).

Geminal ^{199}Hg-C-^{1}H spin-spin coupling in symmetrical dialkylmercurials (190) and in RHgY-type mercury alkyls (191) and ^{199}Hg-C-^{19}F and ^{199}Hg-C-C-^{19}F spin-spin coupling in symmetrical and unsymmetrical perfluoroalkylmercurials (192) have been studied in detail by Fedorov and coworkers. The results were discussed in terms of contributions of resonance and inductive effects of the substituents. In the ^{19}F spectra of polyfluoroalkylmercurials, J(^{199}Hg-C-^{19}F) increases as the number of fluorine substituents on the α-carbon atom increases, and, as Table 19 shows, these coupling constants are solvent-dependent. Further information concerning the dependence of J(^{199}Hg-^{1}H) and J(^{199}Hg-^{13}C) on the dihedral angle in organomercurials was provided by an NMR study of mercurated sugars 53 and 54 (Tables 20 and 21) (193). Note, however, a previous, more extensive study, discussed in last year's Survey: Kitching et al., Tetrahedron Lett. (1975) 759.



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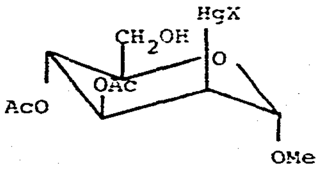

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TABLE 20. J(^{119}Hg-^{1}H) (Hz) for 53 and 54 in $(CD_3)_2CO$.

Compound	H-1	H-2	H-3	H-4
53	30	181	131	17.5
54	84	215	418	11

TABLE 21. $J(^{199}Hg-^{13}C)$ (Hz) for 53 and 54 in $(CD_3)_2CO$.

Compound	C-1	C-2	C-3	C-4	C-5	C-6
53	49.2	1855.5	120.4	225.2	8.2	11.2
54	12.3	1853.7	135.3	53.3	(indeterminate)	

Various proton NMR investigations of CH_3HgY compounds have been reported, in general dealing with the effect of Y and the solvent medium on the CH_3 chemical shift and on $J(^{199}Hg-^{1}H)$.

- Y = SR, OAc, Cl, Br, SCN, CN, $SC(O)CH_3$, $SHgMe_3$ (145)
- Y = NO_3 (oriented in lyotropic nematic media; a study used to determine the C-Hg bond distance) (194).
- Y = NO_3 (^1H and ^{13}C NMR in strong acid) (195).

Two studies of ^{13}C shieldings and $^{199}Hg-^{13}C$ spin-spin coupling constants in phenyl-, alkyl- and alkenylmercury compounds have been published (196, 197). One of these (197) focuses on the solvent-dependence of ^{13}C chemical shifts and of the coupling constants. Typical data are shown in Tables 22, 23, 24 and 25. In the observed spectra of the exo- and endo-isomers of 2-norbornylmercuric bromide the angular dependence of $J(^{199}Hg-^{13}C)$ also was apparent (196).

A pulsed NMR study of σ-cyclopentadienylmercury compounds, C_5H_5HgY (Y - C_5H_5,Cl, Br, I) gave evidence of motion in the solid state, most probably, according to the authors,. "a series of 1,2-shifts of the ring relative to the mercury atom, with simultaneous rotation of the cyclopentadienyl ring together with breaking and reforming of the carbon-mercury σ-bond" (198). Thus we find that these molecules are fluxional not only in solution, but also in the solid state.

C. ESR Spectroscopy

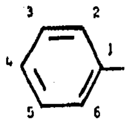
The ESR spectrum of the $\bullet CH_2HgCl$ radical (from γ-irradiation of polycrystalline CH_3HgCl) has been recorded and analyzed (199). The derived value of the ^{201}Hg nuclear quadrupole constant was compared with results of previous studies.

(Continued on p. 293)

TABLE 22. ^{13}C Chemical Shifts of Some Phenylmercury Compounds. From N. K. Wilson, R. D. Zehr and P. D. Ellis, J. Magn. Reson., 21 (1976) 437.

	δ, ppm						
	1	2	3	4	5	6	Other
Phenylmercuric chloride	151.04	136.48	127.94	127.62	127.94	136.48	
Phenylmercuric chloride[b]	148.89	135.67	129.23	129.52	129.23	135.67	
Phenylmercuric chloride[c]	156.8	137.7	129.4	129.4	129.4	137.7	
4-Methylphenylmercuric chloride	147.57	136.17	128.58	136.76	128.58	136.17	20.75 (Me)
4-Methylphenylmercuric chloride[b]	139.49	135.29	129.91	135.29	129.91	135.29	21.23 (Me)
4-Carboxyphenylmercuric chloride	157.46	136.62	128.24	129.83	128.24	136.62	167.13 (C=O)
4-Trifluoromethylphenylmercuric chloride	154.46	133.12	124.11	128.34	124.11	133.12	124.40 (CF_3)
2-Hydroxyphenylmercuric chloride	137.48	159.30	115.07	129.25	119.53	137.20	
Pentachlorophenylmercuric chloride	169.06	126.12	114.69	137.68	114.69	126.12	
Pentafluorophenylmercuric chloride	124.1	165.2	133.5	141.3	133.5	165.2	
Phenylmercuric bromide	154.56	136.46	128.09	127.76	128.09	136.46	
Phenylmercuric acetate	145.14	136.74	127.98	127.78	127.98	136.74	23.32 (Me) 174.80 (C=O)

Phenylmercuric benzoate	145.24	136.79	127.98	127.98	127.98	136.79	169.65 (C=O) 131.35 (C-1') 129.22 (C-2'), 6',3',5', 134.52 (C-4')
Phenylmercuric lactate	145.01	136.76	127.98	127.77	127.98	136.76	178.50 (C=O) 68.12(CHOH) 21.24 (Me)
Di(phenylmercuric)-phthalate	145.38	136.80	128.10	128.10	128.10	136.80	171.77(C=O) 129.01(C1', 6') 127.80(C2', 5') 136.80(C3', 4')
Diphenyl mercury	170.58	137.81	127.55	126.87	127.55	137.81	
Diphenyl mercury[b]	170.00	137.31	128.48	128.10	128.48	137.31	
Diphenyl mercury[c]	168.96	138.61	128.79	128.30	128.79	138.61	
Di(4-methylphenyl)-mercury[b]	166.86	137.04	129.22	137.75	129.22	137.04	21.28 (Me)

[a] Numbering: 

HgR; values reported are for 0.5 M solutions in dimethyl sulfoxide-d_6 unless otherwise noted. Shieldings have a precision of ±0.05 ppm.

[b] Saturated solutions in 1,1,2,2-tetrachloroethane-d_2, except diphenylmercury 0.4M.

[c] Saturated solutions in acetone-d_6.

TABLE 23. ^{199}Hg-^{13}C Coupling Constants in Some Phenylmercury Compounds;[a] From N. K. Wilson, R. D. Zehr and P. D. Ellis, J. Magn. Reson., 21 (1976) 437.

	$^1J_{CHg}$	$^2J_{CHg}$	$^3J_{CHg}$	$^4J_{CHg}$ (Hz)
Phenylmercuric chloride	2634	118.6	209.0	37.1
4-Methylphenylmercuric chloride	2624	123.7	220.8	34.8
4-Carboxyphenylmercuric chloride	2694	124.4	216.6	40.0
2-Hydroxyphenylmercuric chloride	3196	126 (C-2)	118.6 (C-3)	
		72 (C-6)	200.5 (C-5)	
Phenylmercuric acetate	2666	120.4	210.7	37.2
Phenylmercuric benzoate	2728	121.1	214.3	
Phenylmercuric lactate	2714	120.9	212.3	31.4
Di(phenylmercuric)phthalate	2702	122.6	213.8	
Diphenylmercury	1275	84.5	104.1	20.5
Diphenylmercury[b]	1189	85.5	101.0	18.5
Diphenylmercury[c]		87.6	102.0	
Diphenylmercury[d]	1186	88	101.6	17.8
Di(4-methylphenyl)mercury[b]		85.1	106.8	

[a] In dimethyl sulfoxide-d_6 unless otherwise noted. Error estimates are: $^1J \pm 2$ Hz, $^2J \pm 0.6$ Hz, $^3J \pm 0.4$ Hz, $^4J \pm 1.2$ Hz. [b] In 1,1,2,2-tetrachloroethane-d_2. [c] In acetone-d_6. [d] In MeOH or H_2O.

TABLE 24. ^{13}C Chemical Shifts and ^{199}Hg-^{13}C Coupling Constants of Some Alkyl- and Alkenylmercury Compounds. From N. K. Wilson, R. D. Zehr and P. D. Ellis, J. Magn. Reson., 21 (1976) 437.

Compound[a]	δ			
	C-1	C-2	$^1J_{\mathrm{CHg}}$	$^2J_{\mathrm{CHg}}$
Methylmercuric chloride	6.03		1665	
Methylmercuric bromide	9.48		1625	
Methylmercuric iodide	14.89		1543	
Ethylmercuric chloride	22.63	13.66	1689	95.5
Dimethylmercury[b]			692	
Diethylmercury[b]			648	24
Divinylmercury[b]			1159	
Divinylmercury (neat)	169.2	135.0	1161	36.6

[a] Approximately 0.5 M in dimethyl sulfoxide-d_6. Error estimates are: $\delta \pm 0.05$ ppm, $^1J \pm 2$ Hz, $^2J \pm 0.6$ Hz. [b] In MeOH or H_2O.

TABLE 25. ^{13}C Chemical Shifts and ^{199}Hg-^{13}C and ^{199}Hg-^{1}H Coupling Constants of Some MeHgX and PhHgX Compounds. From A. J. Brown, O. W. Howarth and P. Moore, J. Chem. Soc., Dalton Trans. (1976) 1589

(a) HgMeX

X	Solvent	$\delta(^{13}C)$	$^{1}J(C-Hg)$	$^{2}J(H-Hg)$
dmso	$[^{2}H_6]$dmso acidified with CF_3SO_3H	1.4 ppm	1936.9 Hz	260.6 Hz
Me	pure liquid	23.7	692	101
	$[^{2}H_6]$dmso	23.1	725.6	105.1
	$[^{2}H_6]$chloroform	23.4	688.5	101
Water-$[OH]^-$	water, pH 0	0.3	1764	260
	water, pH 1.0	-0.8	1750	
	water, pH 11.5	-0.8	1309	204
$MeCO_2^-$	80% $MeCO_2H$	-1.3	1624	
	water, pH 5.4	-0.5	1629	
	$[^{2}H_6]$dmso	0.8	1695.3	
	pyridine			220.8
Cl^-	$[^{2}H_6]$dmso	8.4	1673.8	221.5
	$[^{2}H_6]$chloroform	8.6	1430.7	203.6

	pyridine			215.2
	dioxan			209
Br^-	$[^2H_6]$dmso	11.7	1630.9	217.7
	$[^2H_6]$chloroform	12.8	1393.6	196.9
	pyridine			212.9
	dioxan			205
I^-	$[^2H_6]$dmso	17.1	1540	208
	$[^2H_6]$chloroform	18.8	1301.3	184
	pyridine			200
CN^-	$[^2H_6]$dmso	4.7		
NCS^-	$[^2H_6]$dmso	0.0	1710	
Tetrahydrothiophen	$[^2H_6]$dmso	0.7	1690	
PPh_3	$[^2H_6]$dmso	1.2	1710	
Glycine	water, pH 7.05	-1.3	1588.4	216
L-2-Phenylalanine	water, pH 6.5	-2.7	1582.5	220
DL-Tyrosine	water, pH 3.66	-3.0	1591.3	
DL-Methionine	water, pH 0.29	5.8	1601.0	
Seleno-DL-methionine	water, pH 0.47	8.6	1510.2	
DL-Cysteine	water, pH 7.8	9.8	1256.8	174

TABLE 25. (Cont'd)

Thioglycolic acid	water, pH 6.8	9.6	1270.0
DL-Penicillamine	water, pH 9.2	8.4	1335.9
$Hg(CH_2Ph)_2$	fused solid		638

(b) HgPhX

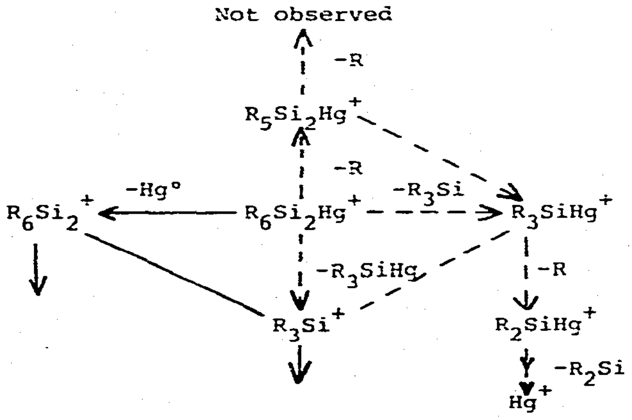
X	Solvent	$\delta(^{13}C)$	$^nJ(C-Hg)$	Ring carbon number (n)
Ph	fused solid(?)	unknown	1186,88	1,2,
			101.6,17.8	3,4
	$[^2H_6]$dmso	172.5,139.7	1275,85.3	
		129.4,128.7	101.5,10(?)	
$MeCO_2^-$	$[^2H_6]$dmso	147.1,138.6	2661.1,119.6	1,2,
		129.9,129.7	210.0,36.6	3,4
	80%$MeCO_2H$	143.0,137.5	127,	1,2
		129.6,129.9	218,36	3,4
	$[^2H_6]$chloroform	144.0,137.7	122	1,2
		130.7,130.4	203,37	3,4
Br^-	$[^2H_6]$dmso	156.4,138.2	122	1,2
		129.9,129.6	206,38	3,4

D. Photoelectron Spectroscopy

The He I photoelectron spectra of a number of symmetrical and unsymmetrical dialkylmercury compounds have been measured (200). The two principal bands observed are due to ionization of electrons from σ bonding orbitals (7.57 eV for di-*t*-butylmercury to 9.33 eV for dimethylmercury) and ionization from the Hg $5d^{10}$ shell (14.4-15.9 eV) (Table 26).

E. Mass Spectroscopy

Further studies of the mass spectroscopic behavior of R_2Hg and RHgX compounds have appeared (201). For all arylmercurials of either type the observed base peak was due to the carbonium ion, R^+, but in the case of CH_3HgX (X = halogen) compounds, it was due to the species $MeHgX^{\dot{+}}$. In the mass spectra of $(Me_3MCH_2)_2Hg$ (M = Si, Ge) and Me_3MCH_2HgX (X = Cl, Br) the principal fragmentation involved Me-M bond cleavage, rather than rupture of the C-Hg bond. Other workers have investigated the mass spectroscopy of organosilylmercurials, $(R_3Si)_2Hg$, including $(Me_nEt_{3-n}Si)_2Hg$, $(Ph_nMe_{3-n}Si)_2Hg$, $(Me_nCl_{3-n}Si)_2Hg$ (n = 0 - 3); $(RMe_2Si)_2Hg$ (R = n-Pr, $PhCH_2$, $CH_2{=}CH(CH_2)_n$ (n = 1-3), Me_3SiCH_2), $[(Me_3Si)_3Si]_2Hg$, $(Me_3C)_2Hg$, $(Me_3Ge)_2Hg$ and $Me_3SiHgGeMe_3$ (202). The extrusion of mercury was found to be the principal process of fragmenttation. The general fragmentation scheme is that shown below.



11. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY

In the reports published in 1976 which dealt with the analysis of organomercurials the following topics were covered:

- The quantitative analysis of organomercurials by mass spectrometry (203).
- The thermogravimetric and GLC determination of some phenylmercury compounds, PhHgX (X = Cl, Br, I, SCN), Ph_2Hg and $(PhHg)_2S$ (204).
- Radiochemical techniques for the determination of $CH_3Hg(II)$ and PhHg(II), based on isotope exchange reactions, e.g.:

$$\text{MeHgCl in 0.5 }\underline{M}\ H_2SO_4 + {}^{203}Hg(NO_3)_2\text{ in 0.4 }\underline{M}\ HNO_3$$

$$\Big\downarrow\ \begin{array}{l}1)\ Ag^+,\ 18\text{-}20h\\ 2)\ \text{concd. HCl}\\ 3)\ \text{benzene}\end{array}$$

The organic layer after this procedure contains $Me^{203}HgCl$ whose activity is measured. The sensitivity goes to 0.01 ppm MeHg(II) (205).

$$\text{MeHgCl in aq. HCl}\ \xrightarrow[\text{extract}]{\text{benzene}}\ \xrightarrow[\text{ascorbic acid}]{\text{KI* in 1\% aq.}}\ \text{MeHgI*}$$

The activity of the organic layer containing the radioactive methylmercuric iodide is measured (206).

The activity of the benzene extracts is measured. The procedure, which allows the determination of PhHg(II) in the presence of MeHg(II), is based on the fact that isotope exchange between radioactive Hg^{2+} and $PhHg^+$ is fast, while that with $MeHg^+$ is very slow (207).

$$\text{PhHgCl + MeHgCl in aq. HCl} + {}^{203}HgSO_4\text{ in 0.5 }\underline{M}\ H_2SO_4$$

$$\Big\downarrow\ \text{extract with benzene}$$

$$Ph^{203}HgCl + MeHgCl$$

TABLE 26. The first and 5d^{10} Vertical Ionization Potentials (eV) of Dialkylmercury Compounds. From T. P. Fehlner, J. Ulman, Q. A. Nugent and J. K. Kochi, Inorg. Chem., 15 (1976) 2544.

Compound	1st IP	5d^{10} IP
$(CH_3)_2Hg$	9.33	14.93
$(CH_3)(C_2H_5)Hg$	8.84	14.85
$(C_2H_5)_2Hg$	8.45	14.71
$(CH_3)(i\text{-}C_3H_7)Hg$	8.48	14.86
$(CH_3)(i\text{-}C_4H_9)Hg$	8.75	14.74
$(CH_3)(t\text{-}C_4H_9)Hg$	8.31	a
$(C_2H_5)(i\text{-}C_3H_7)Hg$	8.18	14.61
$(n\text{-}C_3H_7)_2Hg$	3.29	14.63
$(i\text{-}C_3H_7)_2Hg$	8.03	14.63
$(C_2H_5)(t\text{-}C_4H_9)Hg$	8.06	a
$(i\text{-}C_3H_7)(t\text{-}C_4H_9)Hg$	7.73	a
$(n\text{-}C_4H_9)_2Hg$	8.35	a
$(i\text{-}C_4H_9)_2Hg$	8.30	14.47
$(t\text{-}C_4H_9)_2Hg$	7.57	a
$(i\text{-}C_4H_9)(neo\text{-}C_5H_{11})Hg$	8.33	14.49
$(neo\text{-}C_5H_{11})_2Hg$	8.30	14.41

[a] Band intensity too low for observation above noise level.

- A rapid method for the determination of CH_3HgCl in water samples by GLC using a microwave emission spectrometric detector (208).
- A UV spectrophotometric method for determining inorganic mercury in the presence of methylmercury(II) (209).

- TLC behavior of the mercuration products of acetylenic esters (211).

Arylmercury compounds can serve in the analytical determination of SH groups. Thus, $p\text{-}Et_2NC_6H_4HgOAc$ has been used in the determination of SH in biological samples (212) and sodium o-hydroxymercuribenzoate and sodium p-chloromercuribenzoate have found application in the GLC determination of RSH in petroleum fractions (213..

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